TEXTBOOK OF ELECTROCHEMISTRY

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by

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(abbreviated)

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EXAMPLES

SOLUTIONS TO THE PROBLEMS

IMPORTANT SYMBOLS

a_i Activity of substance i, (II, 169)

Mean activity of an electrolyte (IV, 33)

A Free energy (II, 137)

c Velocity of light

c_i Concentration in mol/litre of a substance i (II, 161)

C Capacity (I, 32)

C_V Heat capacity at constant volume (II, 37)

C_P Heat capacity at constant pressure (II, 42)

ΔC_V Change of heat capacity in a process as described ΔC_p by an equation (II, 62)

D Diffusion coefficient (V, 44)

e Base of natural logarithms

e Electrode potential (VII, 46)

e_0 Standard electrode potential (VII, 48)

e_0^- Electronic charge (VII, 1a)

E Extinction (IV, 20)

E Electromotive force of a cell (VII, 7)

Standard value of e.m.f. (25 °C., 1 atm. pressure) (VII, 9)

f_λ Conductance coefficient (IV, 10)

f_0 Osmotic coefficient (IV, 12)

$f_{(N)}$ Rational activity coefficient (IV, 25)

$f_{(m)}, f_{(c)}$ Practical activity coefficient (IV, 26, 27)

f_u Activity coefficient of uncharged molecules (IV, 41)

F Field strength (I, 17)

F The Faraday

G Free heat content (II, 138)

h PLANCK's constant

H Enthalpy (II, 33)

i Current (I, 1)

I Ionisation energy

$I_{(c)}$ Ionic strength, in terms of volume concentration (IV, 37)

$I_{(m)}$ Ionic strength, in terms of weight concentration (IV, 37)

k BOLTZMANN's constant (V, 6)

k Reaction velocity constant (V, 58)

K Classical equilibrium constant (IV, 23)

K Thermodynamic equilibrium constant (II, 185)

K_A Acidic dissociation constant (IX, 2)

K_B Basic dissociation constant (IX, 5)

K_h Hydrolysis constant (IX, 24)

K_S Solubility constant (IV, 36)

l_i Mobility of an ion i (I, 68)

l_∞ Mobility at infinite dilution (III, 38)

L Latent heat per gram mol (II, 136)

m Concentration in mol/1000 g. of solvent (II, 163)

M Molecular weight

n_i Number of mols of a substance i (II, 162)

n_e Electrochemical valency (I, 56)

$\left. \begin{matrix} n_+ \\ n_- \end{matrix} \right\}$ Transport number (I, 69)

N Molar fraction (II, 162)

N_A AVOGADRO's number

P Pressure

pH Negative decadic logarithm of the $H_3O^{\cdot}$ activity (VIII, 24)

pK Negative decadic logarithm of the thermodynamic dissociation constant (IX, 41)

P Molar polarisation (III, 36)

P Proton affinity (IX, 74)

P Force

P Ionic product of water (VIII, 3)

P_f Frictional force (I, 53)

q Electric charge

r Distance, radius

R Gas constant (II, 15)

R Resistance (I, 1)

S Entropy (II, 104)

t Time

T Absolute temperature

u_i Velocity of migration of an ion i (I, 68)

IMPORTANT SYMBOLS

U Internal energy (II, 14)

v Velocity

V Volume

w Work transfer in a process

$\overline{V}$ Partial molar volume (II, 83)

w' Specialized work transferred in a process

a Degree of dissociation (I, 62a)

a Polarisability (III, 6)

γ Surface tension (X, 1)

δ Diffusion layer thickness (XI, 3)

ε Dielectric constant (I, 35)

ε Molar extinction coefficient (IV, 20)

ζ Electrokinetic potential (X, 45)

η Overpotential (XI, 1)

$\varkappa$ Specific conductance (I, 7)

$1/\varkappa$ Radius of the ionic cloud (V, 14)

λ DONNAN partition coefficient (X, 32)

λ Wave length

Λ_v' Molar conductance (I, 7)

Λ_v Equivalent conductance (I, 64)

Λ_∞ Equivalent conductance at infinite dilution (IV, 3)

μ Dipole moment (III, 1a)

μ_i Chemical potential of a substance i (II, 158)

μ_i Standard chemical potential of a substance i (II, 158)

ν Frequency of radiation

ν Number of ions arising from an electrolyte (I, 56)

$\Delta\pi$ Osmotic pressure (II, 230)

ϱ Density of a solution (II, 164)

ϱ Charge density per cc. (I, 27)

σ Charge density per sq.cm. (I, 26)

ψ Potential (I, 19)

ELECTRICAL PHENOMENA AT INTERFACES

1. Potential Differences at Phase Boundaries

A potential difference always occurs at the interface of two phases containing ions, multipoles or electrons. Some examples of potential differences at phase boundaries and the factors controlling them are (a) a metal dipping into a solution containing its ions, where the potential difference depends on the difference of the chemical potentials of the ions taking part in the processes at the metal-solution interface; (b) liquid junction potentials, which originate from the different mobilities of positive and negative ions; (c) the glass electrode where the potential difference depends on the impermeability of glass to all ions except H_3O^+; (d) the interface between two metals where a contact or Volta potential difference exists owing to the difference in chemical potentials of the electrons in the two metal phases; (e) two immiscible solutions of the same electrolyte in different solvents because the ions are solvated to different degrees, and tend to congregate where the interaction with the solvent is strongest, *i.e.* where the potential energy is least. In all the examples quoted above a stationary state is eventually reached as the resultant potential difference tends to counteract the process causing it.

Phase boundary potentials are complicated by being *dependent on the state of the surfaces of the phases*. For instance, a potential difference may be observed between two solutions which are identical except that one has a capillary active substance [1] at

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[1] A capillary active substance is one which, upon addition to a solution, alters its interfacial tension. The effect on the interfacial tension is due to adsorption of the solute at the interface (see GIBBS adsorption equation). Hence "capillary active substance" means, in its widest sense, a substance which becomes preferentially adsorbed at an interface.

its surface. To produce this effect, substances adsorbed on the surface of the solution must have a dipole at one end of which there is a lyophilic group directed towards the bulk of the solution, as in the higher fatty acids. The layer of oriented dipoles thus produced causes cations and anions to be attracted from the two solutions respectively, and a potential difference between the two phases hence arises, dependent in magnitude on the surface concentration of dipoles. This concentration can be calculated from the lowering of surface tension at the interface.

In accordance with the above, it is found that the potential difference set up at a metal-solution interface depends on the state of the surfaces of the two phases which in turn is a function of the substances present in solution. This is particularly true with respect to the anion, which, being generally more polarisable than the corresponding cation, is usually more easily adsorbed at an nterface.

(i) *Electrocapillary Curves*

The relation between surface properties and potential difference at a liquid metal-solution interface may be examined by means

of *"electrocapillary curves"*, *i.e.* curves of the interfacial tension against the potential of the metal, from which, as shown below, the dependence of charge residing on the metal surface and capacity of the interface on potential can be derived. Knowledge of these relations is useful in establishing the detailed structure of the electrical double layer at the interface (see next section).
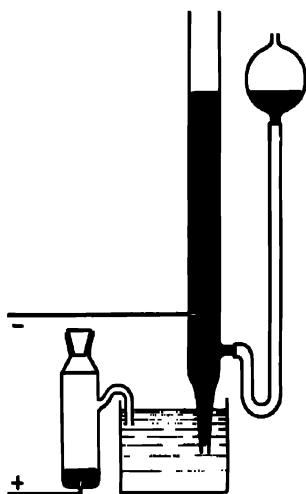
Electrocapillary curves can be determined with a LIPPMANN *capillary electrometer* which is shown diagrammatically in Fig. 49. The most important part of this apparatus is the narrow glass capillary in which the interface between the liquid metal

Fig. 49.
Capillary electrometer

(nearly always mercury) and the solution is formed. The interfacial tension between the mercury and the solution (changes which are indicated by a displacement of the mercury meniscus) depends on the charge and therefore the potential difference at the mercury-solution interface. This is because the charges on the surface mutually repel one another and hence tend to *expand* the surface. It follows that the interfacial tension (which tends to *contract* the surface) is lower the greater the surface charge density, an effect which is independent of the sign of the charge on the electrode, the expanding force of the charge on the mercury surface being proportional to the *square* of the charge density.

Suppose that the electrolyte in contact with the mercury in a LIPPMANN electrometer consists of a solution of sodium sulphate saturated with mercurous sulphate and that $a_{SO_4''} = 1$; then the potential difference at the mercury meniscus corresponds to the normal potential of the $Hg/Hg_2SO_4/SO_4''$ electrode, which is about 0·6 volt on the normal hydrogen scale (according to Table 23). The mercury is positively charged relative to the solution and the state of the electrical double layer can be represented as in Fig. 50a. Owing to the charge present on the surface, the surface tension of the mercury at its interface with the solution is less than the value in the

Fig. 50. Electrical double layers at a solid-solution phase boundary

uncharged state. Now suppose that a gradually increasing negative potential is applied to the mercury, from an external source of e.m.f., then more Hg_2·· ions are discharged and a smaller number of these ions is present at the interface. As a result the potential difference and charge at the mercury-solution interface decrease and the surface tension, γ, rises. When the charge is zero, the value of γ reaches a maximum, there being no longer any expanding effect of charge to decrease the interfacial tension. If the negative polarisation is increased further, an opposite charge arises at the interface, as shown in Fig. 50b and the interfacial tension decreases once more.

An important relation between the charge density of the double

layer, σ, the surface tension, γ, and the potential difference, $\varDelta\psi$, between the two sides of the double layer can be found as follows. In a system containing, say, $Hg_2\cdot\cdot$, SO_4'', $H\cdot$ and OH' ions, and electrons, consider the change of γ with $\varDelta\psi$ at constant sulphuric acid concentration. As the acid strength remains constant, it follows that the $d\mu$ for SO_4'', $H\cdot$ and OH' is zero. Let it be assumed, as a special case, that there is no surface excess or deficit of metallic ions at the interface, *i.e.* that the surface excess of $Hg_2\cdot\cdot$ ions is zero.

This assumption makes the application of the GIBBS adsorption equation (*cf.* "Problems", No. II, 8) to the system particularly easy[1]. The latter equation can be written in the form

$$\varGamma = -\frac{d\gamma}{RT\,d\ln a}\ , \qquad (1)$$

where a is the activity of a given component in solution, the surface tension of the interface is γ, and $\varGamma$ is the excess surface concentration of the component. For several components equation (1) can be written

$$d\gamma = -\varSigma\,\varGamma\,d\mu\ , \qquad (2)$$

where μ is the chemical potential of a component in the system and the summation extends over all the independent variable components of the system. It has already been noted that $d\mu$ for all the ions present is zero for the boundary conditions given above so that only $d\mu$ for the electrons remains and this is given by

$$\varGamma_{\text{electrons}} = -\frac{d\gamma}{d\mu}\ . \qquad (3)$$

Now $\varGamma_{\text{electrons}}$, the excess of electrons in the surface layer, can be replaced by its equivalent in coulombs per sq.cm., σ, if the chemical potential term $d\mu$ is replaced by the equivalent electrical term $d\varDelta\psi$ for the electrons, at constant surface area. Consequently,

$$\sigma = -\frac{\partial\gamma}{\partial(\varDelta\psi)}\ . \qquad (4)$$

Equation (4), which is the general relation between the gradient of the electrocapillary curve and the quantity of electricity per unit area of the double layer, is termed *Lippmann's equation*. The

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[1] See E. K. RIDEAL, *Introduction to Surface Chemistry*, Cambridge, 1930.

function $\gamma = f(\Delta\psi)$ describes the *electrocapillary curve* which can be readily obtained with the capillary electrometer (see page 353). Fig. 51 shows electrocapillary curves for various electrolytes in aqueous solution. If the double layer in Figs. 50a and b is regarded as a charged condenser, the charge density is

$$\sigma = C \, \Delta\psi \,, \tag{5}$$

where C is the capacity of the condenser per sq.cm. Eliminating charge density from (4) and (5) and integrating it follows (assuming C to be constant with changing $\Delta\psi$[1]) that:

$$\gamma = -C/2 \cdot (\Delta\psi)^2 + \text{const.} \tag{6}$$

Hence, for $\Delta\psi = 0$ the surface tension, γ, has the maximum value, γ_0, so that

$$\gamma_0 - \gamma = C/2 \cdot (\Delta\psi)^2 \,. \tag{7}$$

The differential form of this equation is of more general applicability because from it the variation of the capacity of the electrical double layer with potential can be determined from electrocapillary data. From (7) it follows clearly that[2]:

$$\frac{\partial^2 \gamma}{\partial^2 (\Delta\psi)} = C_\psi \,. \tag{8}$$

Equation (7) is the equation for a parabola if $\Delta\psi$ is taken as zero at the position of the maximum surface tension. Tests of this equation show that for some solutions, *e.g.* aqueous potassium nitrate for concentrations $0.001 < c < 1$ gram ion per litre, an almost parabolic electrocapillary curve is in fact obtained and the position of the maximum is roughly independent of the concentration of the electrolyte. This confirms that *for these solutions the double layer can be treated essentially as in the deduction of the above equation*, i.e. *as a charged condenser* (see Fig. 50a and b).

For most solutions, however, the electrocapillary curve is not

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[1] Closer investigation shows that C varies with ψ. Consequently, in addition to the "Capacity", *i.e.* the mean value of C over a range of potentials, another capacity, known as the *Differential Capacity*, is defined by $C_\psi = \dfrac{\partial q}{\partial \psi}$. It represents the value of C at any point in the potential-charge relation.

[2] For more detailed thermodynamic equations concerning the double layer, see D. C. GRAHAME, *J. Chem. Phys.*, 1948, **16**, 1117.

strictly parabolic, but assymmetric, the position of the maximum being lowered and moved to greater or smaller values of $\Delta \psi$ (see Fig. 51). This type of behaviour is always observed when either the cation or the anion is predominantly adsorbed at the interface, *i.e.* when one of the ions in the solution is capillary active. With capillary active *anions* such as I′, the *positive* limb of the electrocapillary curve is the *steeper* and the maximum is displaced to greater $\Delta \psi$ values compared with those obtained in solutions not containing capillary active ions. With capillary active cations such as $N(C_2H_5)_4$, the negative limb of the curve is slightly steeper and the maximum is reached at lower $\Delta \psi$ values. In addition, in the presence of capillary active ions the shape and position of the curve with respect to potential depend strongly on the concentration of the electrolyte.

The *asymmetry* of the electrocapillary curves found in the presence of capillary active electrolytes may be explained in the following way. Let the case of capillary active anions be considered.

Fig. 51. Electrocapillary curves for Hg against various electrolytic solutions

These anions are then adsorbed on the surface of the mercury to an extent such that their negative charge overcompensates the positive charge originally on the surface of the mercury, so that an excess negative charge exists upon the electrode. To compensate for this, a second layer of cations takes up its position opposite the excess anionic layer adsorbed in the double layer at the electrode-solution interface, as shown in Fig. 50c. It can be seen that the interface can no longer be regarded as a simple condenser consisting of a double layer of opposite charges but is actually now a triple layer. It follows that in the presence of adsorbed anions the simple theory given above, which assumes a condenser-like double layer, no longer applies exactly and there-

fore the curves are no longer symmetrical parabolas. The *lowering* of the electrocapillary maximum occurs because, even where there is zero charge on the metal, a net, non-uniform charge, and hence a potential gradient, still exists (in the presence of the above described triple layer) in the solution side of the electrode-solution interface even though the potential gradient in the immediate vicinity of the electrode surface is zero; this charge on this side also influences the interfacial tension thus preventing it from attaining the maximum value for a charge-free interface.

(ii) *Electrocapillary Curves and Single Potentials*

It has already been mentioned (see Chapter VII, Section 6) that accurate values of metal-solution potential differences, or absolute single electrode potentials, are not easily attainable, and some factors connected with their attempted measurement will now be discussed.

In the absence of capillary active ions the double layer appears to behave approximately as a simple condenser (so long as a number of conditions are fulfilled, *e.g.* that the concentration of ions which cross the interface is small). At the electrocapillary maximum, the charge on the metal surface is zero and hence, from the analogy of the condenser, the potential difference across the double layer, *i.e.* across the electrode-solution interface, must be zero. Assuming this to be true, the potential of the electrocapillary maximum in a solution of inactive ions can be taken as a null potential, and, therefore, if the potential of any other electrode, *e.g.* a normal mercurous sulphate electrode, is measured against the potential of a mercury electrode at the electrocapillary maximum, then the e.m.f. of the resultant cell should give the absolute single potential of the normal mercurous sulphate electrode. This is found to be +0·85 volt. The potential of any other electrode, X, may then be measured against the mercurous sulphate electrode, the absolute single potential of which is now known, and the absolute single potential of X can thus be found.

Consider now the properties of the mercury electrode as a null electrode in the presence of capillary active ions. At the electrocapillary maximum the charge on the metal surface is zero but

it has been stated above that in the presence of capillary-active ions it is only the potential gradient in the immediate neighbour-hood of the surface which is zero and that a potential gradient exists further out towards the solution. Thus, in the presence of capillary active (*i.e.* adsorbable) ions, the electrocapillary maximum corresponds to a condition of zero charge on the metal surface but not to zero potential difference across the whole double layer. Hence, the mercury electrode at the electrocapillary maximum cannot function accurately as a null electrode in the presence of such ions.

Although the foregoing indicates that the electrocapillary maximum in solutions of non-capillary active substances is apparently a valid null point it is in practice found to be unsatis-factory for accurate work. Thus, the potential of the maximum differs somewhat in various aqueous solutions, none of which apparently contains capillary active ions. These differences probably arise because no anions are entirely non-capillary active, so-called non-active ions being in fact weakly active. Thus, the description of conditions at the electrocapillary maximum in the presence of adsorbable anions (p. 357) is really essentially the general description for all solutions. It follows that *the electro-capillary maximum never corresponds e x a c t l y to a null po-tential* (but always to a point of zero charge on the metal surface). In solutions of inactive ions, however, it is probably approxi-mately (to within about $\pm$ 0·03 volt) a null potential. Absolute single electrode potentials can thus at the best only be roughly determined [1].

(iii) *The Capacity of the Electric Double Layer*

An important method of gaining knowledge on the structure of the electric double layer is by measurements of the dependence

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[1] Further doubt on the accuracy of determinations of the potential difference between metal and solution from the assumption of a null potential at the electrocapillary maximum arises from the possibility that any potential gradient on the solution side of the double layer brings about dipole orientation on that side, which in turn gives rise to a potential difference which would be contained in the measured "null" potential. There is reason to believe, however, that the potential difference contributed by the oriented dipoles is relatively small.

of charge and capacity of the electrode upon its potential. Most of the work upon this subject has been carried out at the interface mercury-aqueous solutions. The examination of solid metal-solution interfaces is much more difficult because it is not easy to apply the electrocapillary method [1], by which it is possible to calculate the amount of adsorbed capillary active substances on the electrode, and the capacity of the electrode-solution interface at a given potential (see equation 8).

In addition to the electrocapillary method, two other important methods for measuring the dependence of charge and capacity of the electrode-solution interface on potential exist. Firstly, it is possible to follow the potential of an electrode as a function of time during the first fractions of a second during which electricity is passed across the electrode-solution interface. This is most conveniently done by means of a cathode ray oscillograph (see Chapter XIII, p. 533). As the current is maintained constant during the experiment, it is possible to plot the potential of the electrode against the quantity of electricity passed.
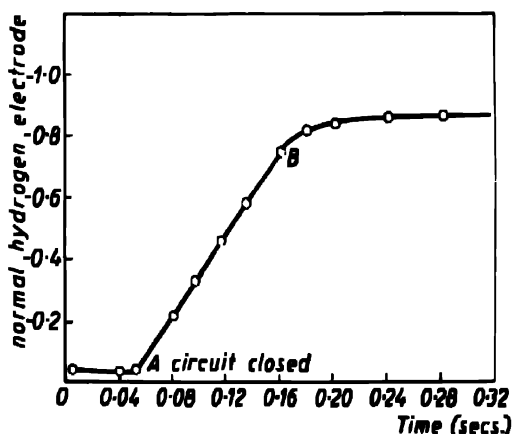
Fig. 52.

Charging curves for a mercury-aqueous acid solution interface

For some electrodes it is found that over a considerable range of potential, the potential/quantity of electricity relation is a linear one (e.g. for the interface mercury-aqueous sulphuric acid, as shown in Fig. 52). The straight line portion AB of Fig. 52 shows that the electrode-solution interface is behaving like a condenser, i.e. the ions (e.g. hydrogen ions in the above

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[1] It is possible to apply QUINCKE's contact angle method for measuring the surface tension of solid-solution interfaces, but the method is insufficiently accurate for application of equation (8).

example) are arriving at the solution side of the double layer but do not cross it (*i.e.* do not discharge and deposit freely on to the mercury electrode as atoms) to any marked extent until the potential has reached a certain value. The capacity of the electrode is given by

$$C = \frac{dq}{d\Delta\psi} = \frac{i\,dt}{d\Delta\psi} \qquad (9)$$

i.e. by the slope of the $\Delta\psi/q$ relation.

This method also makes it possible to determine the *ratio of true to apparent surface area of metals.* It is assumed (a) that metals of the same true areas have the same capacities and (b) that in mercury the true and apparent surface areas are the same. Thus, if the capacity per apparent sq.cm. for the metal M is C_M and that for Hg, C_{Hg}, then the ratio of true to apparent areas is $\dfrac{C_M}{C_{Hg}}$ In this way it is found that smooth, common metals such as Ni, Ag, Cu, *etc.*, have true areas which are up to approximately three or four times greater than their apparent areas; for a given metal this ratio varies with the method of preparation of the surface and with scratched metals and particularly platinized platinum may rise to much higher values.

Fig. 53. The relation of the capacity of the electrode – solution interface to the electrode potential

Alternatively, it is possible to determine the capacity of the electrode-solution interface by introducing it into an A.C. bridge circuit and balancing against a known standard capacity. A D.C. current is superimposed upon the A.C. component and by this means the potential of the electrode-solution interface can be varied at will so that the relation of charge and capacity to

potential can be determined, as with the electrocapillary method. It is also instructive to examine the dependence of the capacity of the double layer upon frequency. When the surface of the electrode is covered with adsorbed atomic hydrogen it is found that there is a variation of the capacity with frequency due to the oscillations of the M-H dipoles in the A.C. field. In metals which do not adsorb hydrogen well, no such variation is found and this probably means that only a very small fraction of the surface of these metals is covered with adsorbed hydrogen atoms [1].

When the charge and capacity of the mercury-dilute aqueous solution interface obtained in this way, or from electrocapillary studies, are plotted against potential, the curve shown in Fig. 53 is obtained. The plateaus C_+ and C_- are identified respectively with the capacities of the electrode-solution interface when the solution side contains cations or anions only. The capacity of the electrode solution interface in the region of potential corresponding to C_+ and C_- is termed the *double layer capacity*, and when this term is used without reservation as to sign it is taken to mean C_+.

It has been found that minute traces of capillary active impurities very largely decrease the capacity of the double layer [2]. Hence, as in measurements of hydrogen overpotential (see p. 418), valid results are difficult to obtain. The value of the capacity of the double layer at the interface mercury-pure dilute aqueous solution can now be accepted as $16 \pm 2\mu F$ per sq.cm.

(iv) *Theory of the Electric Double Layer*

Several detailed theories of the structure of the electric double layer have been proposed. The theory of HELMHOLTZ, in which the double layer was regarded simply as a parallel plate condenser, was followed by that of GOUY who considered the solution side as a diffuse layer of ions in equilibrium with the field of the electrode and the thermal kinetic forces of the solution. The potential-distance relations for these two models are shown in Fig. 54a and b respectively. Neither of these models is satisfactory, the former because it predicts a constant electrode capacity with

[1] P. DOLIN, B. ERSCHLER and A. FRUMKIN, *Acta Physicochim.*, 1940, **13**, 779.

[2] M. PROSKURNIN and A. FRUMKIN, *Trans. Faraday Soc.*, 1935, **31**, 110.
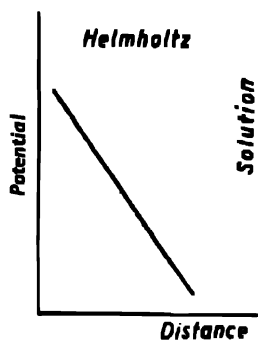
Fig. 54a. HELMHOLTZ'S representation of the potential – distance relation for the electrode – solution interface

Fig. 54b. GOUY'S representation of the potential – distance relation for the electrode – solution interface

change of potential contrary to experiment, and the latter because it does not lead to a connection between capacity and potential which agrees with experiment. At a concentration of $N/10$ the GOUY model gives a double layer capacity of about $250\mu F/cm^2$ at low potentials (*cf.* the experimental value). This discrepancy arises largely from the assumption of the bulk dielectric constant[1] value in the double layer, whereas the actual value will be much less than this owing to dielectric saturation in the vicinity of the electrode. GOUY's model also neglects to take into account the finite size of the ions.

In STERN's theory, which is that most generally used as a model at present, the electrical double layer is regarded as a combination of the compact HELMHOLTZ and diffuse GOUY types. The potential difference be-

Fig. 55. STERN's representation of the potential – distance relation for the electrode – solution interface

[1] *i.e.* the macroscopic dielectric constant as opposed to the dielectric constant near the interface.

tween the electrode and the solution is divided into two parts,
see Fig. 55. Immediately attached to the electrode surface is a
compact layer of thickness equal to that of one ionic layer and
across which is a linear fall of potential, whilst further away
there is a diffuse layer, associated with an exponential fall
of potential, and extending into the bulk of the solution. The
fall across this diffuse part of the double layer is represented by
ψ_1, the potential between the bulk of the solution and the fixed
or HELMHOLTZ section of the double layer.

The potential ψ_1 is sometimes identified with the elektrokinetic
potential, being represented in discussions of surface chemistry
by ζ (it is hence sometimes termed zeta potential). The total
potential difference between the solid phase and the bulk of
the solution is the electrode-solution potential difference, repre-
sented here by $\Delta\psi$.

Let the charge density on the electrode be σ_0, that on the
outer plane of the compact double layer be σ_1, and that on the
diffuse double layer be σ_2. Then,

$$\sigma_0 = \sigma_1 + \sigma_2 . \tag{10}$$

Let n_i be the number of adsorbed ions per sq.cm. of the electrode
surface, $n_{0,i}$ the number of ions of the same type per c.c. in the
bulk of the solution, Z_i the maximum number of ions which can
be adsorbed on one square cm. of the electrode, and $Z_{0,i}$ the
maximum number of ions per c.c. for which there is space
available in the solution. Then, the time spent by an ion on the
surface (t_i) or in the solution $(t_{0,i})$ is proportional to the number
of free spaces at the surface or in solution multiplied by a
BOLTZMANN factor, i.e.,

$$\frac{t_i}{t_{0,i}} = \frac{Z_i - n_i}{Z_{0,i} - n_{0,i}} e^{-w_i/kT} . \tag{11}$$

But, considering all ions of a given type for a short time instead
of one ion for a long time, it is seen that

$$\frac{n_i}{n_{0,i}} = \frac{t_i}{t_{0,i}} = \frac{Z_i - n_i}{Z_{0,i} - n_{0,i}} e^{-w_i/kT} .$$

Solving this equation for n_i, one obtains

$$n_i = \frac{Z_i}{1 + \frac{Z_{0,i}}{n_{0,i}} e^{w_i/kT}} \qquad (12)$$

in dilute solutions (for which $Z_{0,i} \gg n_{0,i}$). It also follows that for such solutions $\frac{n_{0,i}}{Z_{0,i}}$ is approximately the molar fraction of the solute. STERN doubled the 1 of the denominator of (12) in order that for large negative values of w_i, $n_i \rightarrow Z_i/2$ (*i.e.* equal numbers of cations and anions are adsorbed). The term w_i can be written as

$$(w_i)_{\text{Anions}} = z_a e_0 (\psi_1 - \varphi_-), \qquad (13)$$

where φ_- is the adsorption potential of any specifically adsorbed anions, and z_a is the charge on the anion. Correspondingly, for cations,

$$(w_i)_{\text{Cations}} = z_c e_0 (\psi_1 + \varphi_+), \qquad (14)$$

where φ_+ is the specific adsorption potential for the cations, and z_c the charge on the cation.

It follows at once from (12), (13) and (14) that:

$$\sigma_1 = z F \left[\frac{1}{2 + \frac{1}{c} e^{z_a e_0 (\psi_1 - \varphi_-)/kT}} - \frac{1}{2 + \frac{1}{c} e^{z_c e_0 (\psi_1 + \varphi_+)/kT}} \right], \quad (15)$$

where c is $n_{0,i}/Z_{0,i}$.

The charge on the diffuse part of the double layer can be considered using POISSON's equation in a somewhat similar way to that used by DEBYE and HÜCKEL. For a potential varying in one direction only, it is known from POISSON's equation that

$$\frac{d^2\psi}{dx^2} = -\frac{4\pi\varrho}{\varepsilon},$$

where ϱ is the volume charge density at a point x distant from the electrode surface along the X axis, where the electrostatic potential is ψ, and ε is the dielectric constant in the bulk of the solution.

Now,

$$\varrho = \sum n_i z_i e_0,$$
$$= \sum n_{0,i} z_i e_0 e^{-z_i e_0 \psi/kT}.$$

Hence,
$$\frac{d^2\psi}{dx^2} = -\frac{4\pi e_0}{\varepsilon}\Sigma n_{0,i} z_i e^{-z_i e_0 \psi/kT} \quad . \tag{16}$$

Use of the identity
$$\frac{d^2\psi}{dx^2} = \frac{1}{2}\frac{d}{dx}\left(\frac{d\psi}{dx}\right)^2$$

allows (16) to be integrated and gives rise to

$$\left(\frac{d\psi}{dx}\right)^2 = \frac{8\pi kT}{\varepsilon}\Sigma n_{0,i}\left(e^{-z_i e_0 \psi/kT} + A\right) \quad . \tag{17}$$

In the bulk of the solution $d\psi/dx = 0$ and $\psi = 0$. Applying these conditions to equation (17) shows that $A = -1$. Also, from GAUSS's theorem,

$$\frac{d\psi}{dx} = -\frac{4\pi\sigma_2}{\varepsilon} \quad .$$

Hence, from this and (17),

$$\sigma_2 = \sqrt{\frac{\varepsilon kT}{2\pi}\Sigma n_{0,i}\left(e^{-z_i e_0 \psi_1/kT} - 1\right)} \quad , \tag{18}$$

where ψ becomes ψ_1 so that σ_2 represents the charge on the whole diffuse layer.

Thus, from (10), (15), (18) and the equation for the charge on the electrode, $\sigma_0 = \dfrac{\varepsilon'}{4\pi\delta}(\Delta\psi - \psi_1)$ (where ε' is the mean dielectric constant in the HELMHOLTZ double layer and δ is the thickness of this layer), the basic equation of STERN's theory becomes

$$\frac{\varepsilon'}{4\pi\delta}(\Delta\psi - \psi_1) = zF\left[\frac{1}{2 + \dfrac{1}{c}exp\left\{\dfrac{z_e e_0(\psi_1 - \varphi_-)}{kT}\right\}}\right.$$
$$\left. - \frac{1}{2 + \dfrac{1}{c}exp\left\{\dfrac{z_e e_0(\psi_1 + \varphi_+)}{kT}\right\}}\right]$$
$$+ \sqrt{\frac{\varepsilon kT}{2\pi}\Sigma n_{0,i}\left(e^{-z_i e_0 \psi_1/kT} - 1\right)} \quad . \tag{19}$$

As will be seen in Chapter XI, it is important to obtain a relation between ψ_1 and c. In some systems specific adsorption of ions can be neglected and when this is so (e.g. at the interface mercury-dilute aqueous solution of an acid such as hydrochloric)

it follows that:

$$\frac{\varepsilon'}{4\pi\delta}(\Delta\psi - \psi_1) = F z\, c_{\mathrm{H}^{\cdot}} \cdot \left(e^{-z_i \epsilon_0 \psi_1/kT} - e^{z_i \epsilon_0 \psi_1/kT} \right)$$
$$- \sqrt{\frac{RT\,\varepsilon}{2\pi}}\left(c_{\mathrm{H}^{\cdot}}\right)^{\frac{1}{2}}\left(e^{-z_i \epsilon_0 \psi_1/kT} - 1\right)^{\frac{1}{2}}.$$

Except near the electrocapillary maximum, $\Delta\psi \gg \psi_1$ and $e^{-z_i \epsilon_0 \psi_1/kT} \gg 1$. It follows that:

$$\frac{\varepsilon'\,\Delta\psi}{4\pi\delta} = F z\, c_{\mathrm{H}^{\cdot}} \cdot e^{-z_i \epsilon_0 \psi_1/kT} - \sqrt{\frac{RT\,\varepsilon}{2\pi}}\left(c_{\mathrm{H}^{\cdot}}\right)^{\frac{1}{2}} e^{-z_i \epsilon_0 \psi_1/kT}.$$

This equation can be regarded as a quadratic in $(c_{\mathrm{H}^{\cdot}} \cdot e^{-z_i \epsilon_0 \psi_1/kT})^{\frac{1}{2}}$. Solution of this equation shows that $c_{\mathrm{H}^{\cdot}} \cdot e^{-z_i \epsilon_0 \psi_1/kT}$ has one real value from which

$$\psi_1 = \frac{RT}{z_i F} \ln c_{\mathrm{H}^{\cdot}} + \mathrm{const.}$$

The above detailed theory of the electrical double layer has been successful in explaining the form of the experimentally known dependence of charge density and capacity (obtained as described above) on potential, [1] and many other observed relations.

(v) *Membrane Potentials*

The field of membrane equilibria which is of particular importance in colloid and protein chemistry, will now be briefly described (*cf.* p. 291). When a membrane is impermeable to one of a number of ionic species, ionic diffusion through the membrane sets up a difference in ionic distribution on its two sides and a potential difference arises. A simple system can be considered, *e.g.* a solution of a salt of a strong base containing $R^{\cdot}$ and Cl' ions, the solution being separated from a solution of hydrochloric acid by a membrane impermeable to $R^{\cdot}$, *i.e.*,

$$\mathrm{I} \quad \begin{array}{c|c} R^{\cdot}\,Cl' & H_3O^{\cdot}Cl' \\ H_2O & H_2O \end{array} \quad \mathrm{II} \,. \qquad (20)$$
$$M$$

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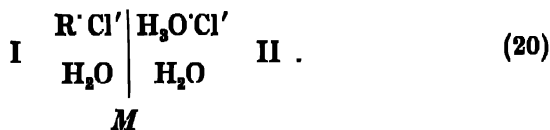
[1] A more detailed treatment of ionic distribution at an interface is given by J. T. DAVIES and E. K. RIDEAL, *J. Colloid Sci.*, 1948, **3**, 313.

The equilibrium condition according to (II, 198) is $d(G_I + G_{II}) = 0$, which means that the chemical potentials of each of the entities present in both phases are equal, *i.e.*

$$\mu^I_{H_3O^+} = \mu^{II}_{H_3O^+}; \quad \mu^I_{Cl'} = \mu^{II}_{Cl'}; \quad \mu^I_{H_2O} = \mu^{II}_{H_2O} \ . \tag{21}$$

Corresponding equations apply when other entities to which the membrane is permeable are present. To establish the equilibrium, H_3O^+ ions must be transferred from II to I, so that correspondingly an exchange of Cl' ions and H_2O molecules takes place between the two solutions until equilibrium is reached. A difference in osmotic pressure $\pi_{II} - \pi_I = \Delta\pi$ will occur if a membrane permeable to the solvent is introduced between phases I and II (*cf.* the case of equilibrium between a solution and the pure solvent, p. 89). In the system considered here, however, an electric potential difference $\Delta\psi$ also exists between both phases because the entities crossing the membrane are charged. If the expression (II, 161) is used to substitute for μ and the pressure dependence of chemical potential is taken into account, then the resulting condition for the equilibrium of water between the two phases at the same temperature becomes (neglecting compressibility of the solution),

$$V_{H_2O} \left(\pi_{II} - \pi_I \right) = RT \cdot \ln \frac{a^I_{H_2O}}{a^{II}_{H_2O}} \ , \tag{22}$$

and correspondingly for both ionic species, application of (VII, 45) gives

$$V_{H_3O^+} \left(\pi_{II} - \pi_I \right) - RT \cdot \ln \frac{a^I_{H_3O^+}}{a^{II}_{H_3O^+}} = \Delta\psi \cdot F \ , \tag{23a}$$

and

$$V_{Cl'} \left(\pi_{II} - \pi_I \right) - RT \cdot \ln \frac{a^I_{Cl'}}{a^{II}_{Cl'}} = -\Delta\psi \cdot F \ . \tag{23b}$$

In the above, the symbol V denotes the partial molar volume of the relevant entity and $\Delta\psi$ is the potential difference set up between the two phases, *i.e.* the membrane potential. By eliminating $\Delta\psi$ from both equations (23a) and (23b), then

$$\pi_{II} - \pi_I = \frac{RT}{V_{H_3O^+} + V_{Cl'}} \cdot \ln \frac{a^I_{H_3O^+} \cdot a^I_{Cl'}}{a^I_{H_3O^+} \cdot a^{II}_{Cl'}} \ , \tag{24}$$

and if $\Delta\pi$ is eliminated between (22) and (24) the final condition

for the membrane equilibrium of system (20) is

$$\frac{1}{V_{H_2O}} \cdot \ln \frac{a_{H_2O}^{I}}{a_{H_2O}^{II}} = \frac{1}{V_{H_2O^{\cdot}} + V_{Cl'}} \cdot \ln \frac{a_{\pm}^{I2}}{a_{\pm}^{II2}} , \qquad (25)$$

which may also be written as

$$\frac{a_{\pm}^{II2}}{a_{H_2O}^{II\varphi}} = \frac{a_{\pm}^{I2}}{a_{H_2O}^{I\varphi}} \qquad (26)$$

where φ represents the ratio of the partial molar volumes of electrolyte and solvent, i.e.,

$$\varphi = \frac{V_{H_2O^{\cdot}} + V_{Cl'}}{V_{H_2O}} . \qquad (27)$$

As mentioned before, the compressibility of both solutions has been neglected in the pressure range $\Delta\pi$. If the solutions are very dilute the value of a_{H_2O} can be taken as unity in both phases and therefore

$$a_{\pm}^{II} = a_{\pm}^{I} . \qquad (26a)$$

Hence, at equilibrium the mean activity of hydrochloric acid must be the same in both phases although the single activities $a_{H_2O^{\cdot}}$ and $a_{Cl'}$ will be different, and therefore,

$$a_{H_2O^{\cdot}}^{II} / a_{H_2O^{\cdot}}^{I} = a_{Cl'}^{I} / a_{Cl'}^{II} . \qquad (26b)$$

If $\Delta\pi$ is eliminated among (22), (28a) and (28b) the membrane potential $\Delta\psi$ is obtained as

$$\Delta\psi = \frac{RT}{F} \cdot \ln \frac{a_{H_2O^{\cdot}}^{II}}{a_{H_2O^{\cdot}}^{I}} \cdot \frac{a_{H_2O}^{I\varphi+}}{a_{H_2O}^{II\varphi+}} = \frac{RT}{F} \cdot \ln \frac{a_{Cl'}^{I}}{a_{Cl'}^{II}} \cdot \frac{a_{H_2O}^{II\varphi-}}{a_{H_2O}^{I\varphi-}} . \qquad (28)$$

Here, φ_+ is used for $\dfrac{V_{H_2O^{\cdot}}}{V_{H_2O}}$ and φ_- for $\dfrac{V_{Cl'}}{V_{H_2O}}$. If a_{H_2O} is taken as the same in both solutions then a normally adequate approximation for $\Delta\psi$ is given by

$$\psi = \frac{RT}{F} \cdot \ln \frac{a_{H_2O^{\cdot}}^{II}}{a_{H_2O^{\cdot}}^{I}} = \frac{RT}{F} \cdot \ln \frac{a_{Cl'}^{I}}{a_{Cl'}^{II}} . \qquad (28a)$$

Single ion activities occur in (28) as in the equations for the e.m.f.'s of cells with diffusion potentials. The mean ionic activities can be accurately substituted for the single ion activities only in

the DEBYE-HÜCKEL concentration range. According to (VII, 87) an e.m.f. identical with that given by (28a) would be observed if the solutions I and II above considered were made up into the following cell containing a KCl bridge to suppress the diffusion potential:

$$\text{(Pt) H}_2 \mid \text{Solution I} \mid \text{KCl} \mid \text{Solution II} \mid \text{H}_2 \text{ (Pt)} . \qquad (29)$$

Such a cell is a concentration cell with respect to $H_3O^\cdot$ ions, and the same results would be obtained if the hydrogen electrodes were replaced by Ag-AgCl electrodes (a concentration cell with respect to Cl' ions). On the other hand the cell

$$\text{(Pt) H}_2 \mid \text{Solution I} \underset{M}{\mid} \text{Solution II} \mid \text{H}_2 \text{ (Pt)} , \qquad (30)$$

where M is a semi-permeable membrane, would have an e.m.f. of zero because in the presence of the membrane the system is in equilibrium and no change in concentration and hence no change in free heat content is involved. This last statement means that there must be a potential difference at the membrane which is equal to the difference between the two single electrode potentials in cell (30) and from (VII, 87) this is

$$\frac{RT}{F} \cdot \ln \frac{a_{H_3O^\cdot}^{II}}{a_{H_3O^\cdot}^{I}} .$$

The membrane potential in the system (20) can therefore be obtained if, after equilibrium has been established, the pH values of both solutions are measured separately against a reference electrode in the same solution and the resulting $H_3O^\cdot$ activities are substituted into (28a). Using the silver-silver chloride electrode $\Delta\psi$ can also be obtained from measurements of the Cl' activities in both solutions. In general, the membrane potential is given by the relation

$$\Delta\psi = \frac{RT}{zF} \cdot \ln \frac{a_i^{II}}{a_i^{I}} , \qquad (31)$$

where a_i is the activity of a z-valent ion of type i to which the membrane is permeable. In the presence of ions of different valencies, the appropriate equilibrium conditions become from (26a)

$$\frac{a_{C^{\cdot}}^{II}}{a_{C^{\cdot}}^{I}} = \frac{a_{A'}^{I}}{a_{A'}^{II}} = \sqrt{\frac{a_{C^{\cdot\cdot}}^{II}}{a_{C^{\cdot\cdot}}^{I}}} = \sqrt{\frac{a_{A''}^{I}}{a_{A''}^{II}}} = \sqrt[3]{\frac{a_{C^{\cdot\cdot\cdot}}^{II}}{a_{C^{\cdot\cdot\cdot}}^{I}}}, \text{etc.}, = \lambda \ . \quad (82)$$

The quantity λ is known as the DONNAN distribution coefficient.

In the above derivation of the equilibrium condition it has been assumed that C' is an ion of a strong base the degree of dissociation of which is independent of *p*H changes in the solution. When the substances to which the membrane is impermeable are weak acids and bases and ampholytes such as proteins, however, dissociation constants have to be taken into account in the calculation of membrane equilibrium. Consider the case of the salt of a weak base, the cation of which can be regarded as the acid RH' (see p. 318). The system is

$$
\begin{array}{c|cc}
\text{RH}^{\cdot} & R & \text{H}_3\text{O}^{\cdot} \text{ Cl}' \\
\text{I} \quad \text{H}_3\text{O}^{\cdot} & & \text{H}_2\text{O} \qquad \text{II} \ . \\
\text{Cl}' & \text{H}_2\text{O} & \\
& M &
\end{array}
\qquad (83)
$$
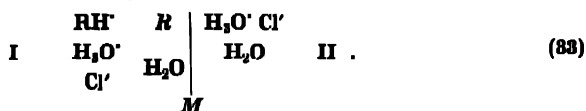
In solution I the dissociation equilibrium (IX, 23) is

$$\text{RH}^{\cdot} + \text{H}_2\text{O} \rightleftarrows \text{H}_3\text{O}^{\cdot} + \text{R}$$
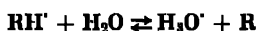
and neither RH' nor R can pass through the membrane.

To find out approximately how the membrane equilibrium is affected by the dissociation equilibrium of the cationic acid, activity coefficients may be neglected. Let the total concentration of salt be c_0.

From (26b) the condition for membrane equilibrium is

$$(c_{\text{H}_3\text{O}^{\cdot}} \cdot c_{\text{Cl}'})_{\text{I}} = (c_{\text{H}_3\text{O}^{\cdot}} \cdot c_{\text{Cl}'})_{\text{II}} = (c^2_{\text{H}_3\text{O}^{\cdot}})_{\text{II}} \ . \qquad (84)$$

In solution I,

$$c_{\text{R}} = c_0 - c_{\text{RH}^{\cdot}} \ ,$$

and the dissociation constant of the cationic acid (which is the hydrolysis constant of the salt) is given by

$$K_h = \frac{c_{\text{H}_3\text{O}^{\cdot}} \cdot c_{\text{R}}}{c_{\text{RH}^{\cdot}}} = \frac{c_{\text{H}_3\text{O}^{\cdot}} \cdot (c_0 - c_{\text{RH}^{\cdot}})}{c_{\text{RH}^{\cdot}}} \ ,$$

from which

$$c_{\text{RH}^{\cdot}} = \frac{c_0 \cdot c_{\text{H}_3\text{O}^{\cdot}}}{K_h + c_{\text{H}_3\text{O}^{\cdot}}} \ .$$

But, from the condition of electroneutrality,

$$c^{\text{I}}_{\text{Cl}'} = c_{\text{H}_3\text{O}^{\cdot}} + c_{\text{RH}^{\cdot}} = c_{\text{H}_3\text{O}^{\cdot}} + \frac{c_0 \cdot c_{\text{H}_3\text{O}^{\cdot}}}{K_h + c_{\text{H}_3\text{O}^{\cdot}}} \ .$$

When the expressions obtained above are substituted in (34),

$$(c^2_{\text{H}_3\text{O}^{\cdot}})_{\text{II}} = \left[c_{\text{H}_3\text{O}^{\cdot}} \left(c_{\text{H}_3\text{O}^{\cdot}} + \frac{c_0 \cdot c_{\text{H}_3\text{O}^{\cdot}}}{K_h + c_{\text{H}_3\text{O}^{\cdot}}} \right) \right]_{\text{I}} \ ,$$

or   (85)

$$c^{\text{II}}_{\text{H}_3\text{O}^{\cdot}} = \left(c_{\text{H}_3\text{O}^{\cdot}} \sqrt{1 + \frac{c_0}{K_h + c_{\text{H}_3\text{O}^{\cdot}}}} \right)_{\text{I}} \ .$$

The DONNAN distribution coefficient therefore becomes,

$$\lambda = \frac{c_{H_3O^\cdot}^{II}}{c_{H_3O^\cdot}^{I}} = \sqrt{1 + \frac{c_0}{K_h + c_{H_3O^\cdot}^{I}}} \ , \tag{36}$$

and the membrane potential is

$$\Delta\psi = \frac{RT}{F} \cdot \ln \sqrt{1 + \frac{c_0}{K_h + c_{H_3O^\cdot}^{I}}} \ . \tag{37}$$

Hence, increasing acidity of the solution causes λ to approach unity and $\Delta\psi$ zero.

Consider now a system containing the salt of a weak acid HA, the membrane being impermeable to both the acid and the anion, and the other side of the membrane being in contact with a KOH solution, i.e.,

$$\text{I} \quad \begin{array}{cc} \text{HA} & \text{A}' \\ \text{OH}' & \text{H}_2\text{O} \\ \text{K}^\cdot & \end{array} \ \bigg| \ \begin{array}{cc} \text{K}^\cdot & \text{OH}' \\ & \text{H}_2\text{O} \end{array} \quad \text{II} \ . \tag{38}$$

$$M$$
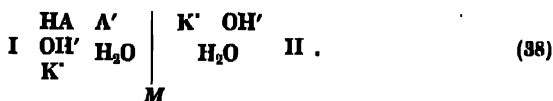
The membrane equilibrium in this case will be affected by the hydrolysis of the salt. If the total concentration of the salt is represented by c_0, then a calculation analogous to that above leads to the expression

$$\lambda = \frac{c_{OH'}^{I}}{c_{OH'}^{II}} = \frac{1}{\sqrt{1 + \frac{c_0}{K_h + c_{OH'}^{I}}}} \ , \tag{39}$$

in which K_h is the hydrolysis constant of the salt corresponding to the reaction

$$\text{A}' + \text{H}_2\text{O} \rightleftharpoons \text{HA} + \text{OH}' \ .$$

Here, λ is less than 1; with decreasing acidity (i.e. increasing OH' concentration) of the solution, it approaches 1 and the membrane potential $\Delta\psi$ approaches zero.

Finally, consider a protein solution near the isoelectric point where both the following equilibria (associated with dissociation constants of K_1 and K_2 respectively) affect the membrane equilibrium (see IX, 34 and 35),

$$\text{RH}^\cdot + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^\cdot + \text{R}'' \ ,$$

$$\text{R}'' + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^\cdot + \text{R}' \ .$$
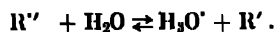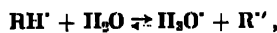
The equilibrium system can be represented by

$$\text{I} \quad \begin{array}{ccc} \text{RH}^\cdot & \text{R}'' & \text{R}' \\ & \text{H}_3\text{O}^\cdot & \text{Cl}' \\ & \text{H}_2\text{O} & \end{array} \ \bigg| \ \begin{array}{cc} \text{H}_3\text{O}^\cdot & \text{Cl}' \\ & \text{H}_2\text{O} \end{array} \quad \text{II} \ . \tag{40}$$

$$M$$
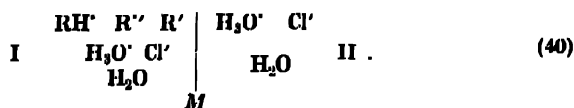
The membrane is impermeable to RH', R'', and R' and the total concentration of ampholyte is c_0. In this case the following relations are applicable :

$$c_{Cl'}^{I} = c_{H_3O^\cdot} + c_{RH^\cdot} - c_{R'} \ . \quad \text{(Condition of electroneutrality)}$$

$$c_{R''} = c_0 - c_{RH^\cdot} - c_{R'} \ .$$

$$K_1 = \frac{c_{H_3O^\cdot} \, c_{R''}}{c_{RH^\cdot}} \ ; \quad K_2 = \frac{c_{H_3O^\cdot} \, c_{R'}}{c_{R''}} \ .$$

Eliminating $c_{R'}$, $c_{RH^\cdot}$ and $c_{R'}$ from the above equations, the Cl' concentration is given by

$$c_{Cl'}^{I} = c_{H_3O'} + \frac{c_0 \left(c_{H_3O'}^2 - K_1 \cdot K_2 \right)}{K_1 \cdot K_2 + K_1 \cdot c_{H_3O'} + c_{H_3O}^2} .$$

Substituting again in the equilibrium condition (34) the DONNAN distribution coefficient is found to be

$$\lambda = \frac{c_{H_3O'}^{II}}{c_{H_3O'}^{I}} = \sqrt{1 + \frac{c_0 \left(c_{H_3O'}^{I2} - K_1 \cdot K_2 \right)}{c_{H_3O'}^{I} (K_1 \cdot K_2 + K_1 \cdot c_{H_3O'}^{I} + c_{H_3O'}^{I2})}} . \qquad (41)$$

It follows from (IX, 43) that at the isoelectric point, and neglecting activity coefficients, $c_{H_3O'}^2 = K_1 \cdot K_2$, so that $\lambda_{isoelec.} = 1$. The membrane potential is therefore zero. On the acid side of the isoelectric point, $c_{H_3O'}^2 > K_1 \cdot K_2$ and λ initially increases with decreasing pH. For sufficiently high values of $c_{H_3O'}$, $K_1 \cdot K_2$ may be neglected and (41) simplifies to

$$\lambda = \sqrt{1 + \frac{c_0}{K_1 + c_{H_3O'}^{I}}} , \qquad (41a)$$

which is the same as (36). At suitably low values of pH, λ must therefore decrease and finally reach unity, i.e. both λ and $\Delta\psi$ pass through a maximum with change of pH. Conversely, on the alkaline side of the isoelectric point $c_{H_3O'}^2 < K_1 \cdot K_2$ and $\Delta\psi$ is negative, i.e. the membrane potential changes sign and increases with increasing pH, passes through a maximum, and approaches zero again when the solution becomes strongly alkaline. These theoretical predictions are confirmed by experiment as is clear from Fig. 56 where membrane potentials for 1% gelatine solution against solutions of several univalent acids are shown as a function of pH. The membrane potential is independent of the nature of the acid and at the isoelectric point $(p_I = 4 \cdot 8)$ is zero. At $pH \approx 4 \cdot 0$ it reaches a maximum and decreases with increasing acidity to zero.

■ = Acetic acid   △ = Lactic acid
○ = HI   □ = HCl
△ = HNO₃   + = Propionic acid
× = HBr
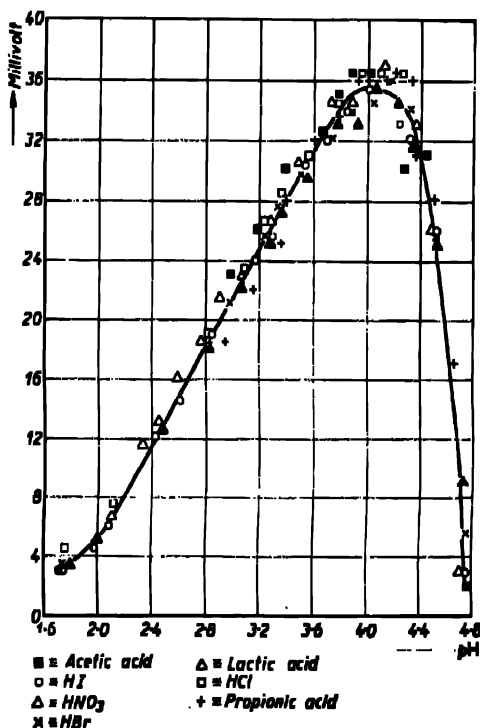
Fig. 56. Membrane potentials of 1% gelatine solutions against dilute solutions of univalent salts as a function of pH

Membrane potentials have considerable importance in biological processes and have added much to our knowledge

of proteins. For instance, the mechanism of the exchange and distribution of inorganic ions between blood corpuscles and blood serum has been elucidated from the viewpoint of the membrane equilibria which are set up at the cell walls. The cells have been found to be impermeable to all inorganic cations except $H_2O^.$, but are permeable to anions. The distribution of electrolytes between blood serum and other body fluids is also governed by membrane equilibria, for the walls of the capillary blood vessels are impermeable to proteins of blood serum, but are permeable to inorganic ions.

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2. Electrical Charges on Colloids

Colloids in aqueous systems can be divided into two groups termed *hydrophilic* and *hydrophobic*. The first class, to which belong the proteins, has a great affinity for water as is shown by their swelling and hydration properties. They form thermodynamically stable systems with water. On the other hand, hydrophobic colloids are in a labile equilibrium, and hence can be flocculated irreversibly by, say, the addition of a small amount of an electrolyte [1]. They have little affinity for water and are practically insoluble in a molecularly dispersed form.

The high stability of solutions of *hydrophobic colloids* may be understood by considering the migration of the particles in an electric field (see p. 882) which indicates that the charges on them are of like sign. The charge on each particle is usually high, so

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[1] There are, of course, cases intermediate between the two extremes where hydrophobic colloids do not behave completely irreversibly on precipitation, but may be partially or even completely returned to the colloidal state by addition of water (peptisation). Colloids belonging to this group contain molecules which, although normally insoluble in water, possess groups which give rise to specific interactions with water, and thus facilitate reversible sol formation.

that considerable repulsive forces are effective at comparatively large distances. Since the dispersion forces (p. 109), which form a large component of the attractive intermolecular forces between the particles, have a much smaller range, the potential energy curve of the net interaction passes through a maximum with distance from the particle and not through a minimum as in the attractive coulombic interaction between ions of opposite sign shown in Fig. 15. Thus, predominance of the repulsive forces prevents the coagulation of the colloid particles and ensures their stability.

It is more difficult to describe the *mechanism of the charging of colloidal particles*, and the precipitation phenomena brought about by addition of neutral salts to colloidal solutions. The types of behaviour shown can be best understood if colloidal solutions are treated as heterogeneous systems, where the colloid particles are the solid phase and give rise to an interfacial potential difference, similar to that between an electrode and a solution, which depends in magnitude on the type and concentration of the ions present in the solutions. For example, if to a 10^{-3} molar potassium iodide solution is slowly added a 10^{-1} molar solution of silver nitrate with vigorous stirring, a silver iodide sol is formed. The silver iodide particles are negatively charged and migrate to the anode under the influence of an electric field. Just before the equivalence point is reached (at $c_{1'} \cong 10^{-10}$) the solution clears and silver iodide is precipitated without any further addition of silver nitrate. Conversely, if a potassium iodide solution is added to a dilute silver nitrate solution, the silver iodide particles are positively charged and migrate to the cathode. Precipitation then occurs near the equivalence point at $c_{Ag'} \cong 10^{-6}$, *i.e.* earlier than in the presence of excess iodide ions. These observations illustrate that negative particles arise in the presence of excess negative ions and positive particles with excess positive ions. It is also clear that I′ ions are more strongly bound by the colloidal particles than the Ag˙ ions, and it must be assumed that the excess I′ or Ag˙ ions are absorbed into the silver iodide lattice [1], so that the solid silver iodide phase is analogous to an electrode which has a definite equilibrium potential in a solution

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[1] The crystalline nature of the colloidal particles has been demonstrated by X-ray and electron diffraction measurements.

of its ions. Similar behaviour is observed with other sparingly soluble salts and hydroxides, where OH' ions determine the potential. For example, the charge on a chromium hydroxide sol depends on the OH' concentration in the solution. If the activity of the ions determining the interfacial potential at the colloid particle-solution interphase is a_i, and the mass of these ions taken up by the disperse phase in the formation of the double layer is $\Delta\gamma_i$ per mol, then the empirical relation between $\Delta\gamma_i$ and a_i is

$$\Delta\gamma_i = k \cdot \Delta\ln a_i, \qquad (42)$$

where k is a proportionality factor [1].

Apart from interchange of "potential-determining" ions between colloidal particles and solutions, adsorption of foreign particles on the colloid particles also occurs in many cases. The forces involved in this adsorption may be of various types between the extremes of true chemical binding and weak intermolecular interaction forces. The adsorption isotherm which is applicable embodies two logarithmic terms, as is often found for non-electrolytes, and may be written

$$\Delta\log\gamma_2 = \frac{1}{n} \cdot \Delta\log c_i, \qquad (43)$$

where $1/n$ is an empirical constant (FREUNDLICH adsorption isotherm). In contrast with the behaviour expressed by (42), the *logarithm* of the amount of adsorbate here varies linearly with the logarithm of the equilibrium concentration in the solution. Adsorption on colloid particles of capillary active ions which do not determine the true potential, may cause change of sign on the colloid particle, or displacement of some of the ions of the disperse phase, so that the conditions influencing the phenomena can become complicated.

Since the stability of hydrophobic colloids has been seen to be due to the electric charge on the colloid particles and this charge is influenced by the adsorption of ions from the solution, it is now possible to consider the mechanism of the characteristic pre-

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[1] The change in concentration of the solution after equilibrium with the solid phase has been established is measured by some sensitive method, *e.g.* a conductometric or photometric one. The quantity of adsorbate on the solid phase may also be obtained directly by using radioactive indicator ions.

cipitation[1] of disperse systems of this kind by electrolytes. General quantitative laws governing precipitation by electrolytes are difficult to establish because the charges on the micelles and the accompanying double layer are of a complex nature. Many theories attempting to relate flocculation to some physical property of colloids have been proposed, but hitherto no general relation to account for all the empirical observations has been found. If, as suggested above, it is possible to regard colloidal particles as a heterogeneous disperse system with a definite phase boundary potential between solid and liquid phases, then the simpler *processes in the precipitation of hydrophobic colloids* by electrolytes can be discussed in the following way.

The simplest view, and one held for a long time, was that electrolytic coagulation of colloids was due to the charge on the micelles being wholly or partially neutralised by adsorption of gegenions[2]. Since the stability of the colloid particles is controlled by their mutual coulombic repulsion, neutralisation of these charges on each particle results in coagulation and precipitation of the colloid caused by the VAN DER WAALS attractive forces. In support of this, ampholytes are found to be most easily coagulated at the isoelectric point where Zwitter ions, which have zero total charge, predominate (see p. 820). According to this adsorption theory electrolytic flocculation is explained by postulating that the charges in the double layer undergo change and cause a corresponding fall in the interfacial potential difference between colloidal particles and solution.

However, the above theory breaks down in many cases. For instance, it is found that each electrolyte causes flocculation[3] at a characteristic threshold concentration which is strongly dependent on the valency of the gegenions of the added salts. It is found empirically that threshold concentrations of 1-, 2-, and

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[1] The terms precipitation, coagulation, flocculation, have approximately the same significance when referring to colloidal systems.
[2] The term gegenions here denotes all ions of charge opposite to that of the micelles.
[3] As flocculation is a slow process, threshold concentrations are not well defined. Accurate photoelectric measurements of turbidity as a function of the concentration of the electrolyte enable calculation of comparable threshold concentrations to be made (see H. A. WANNOW, *Koll. Z.* 1938, **85**, 832, *Koll. Beih.*, 1939, **50**, 375).

8-valent ions are in the ratio 500 : 50 : 1 and that there is also some (much smaller) effect of the ions of the same sign as that of the colloid particle. The characteristic influence of the valency of the gegenion can only be explained on the above adsorption theory of flocculation by assuming that the various ions are adsorbed to approximately the same extent; for, since the interfacial potential difference varies logarithmically with the concentration γ_i of the adsorbed ions,then the fall in potential difference must be a logarithmic function of c_i (the concentration of ions in the solution). As the adsorption of foreign ions is a specific process depending on intermolecular forces, it would hardly be expected that all ions would be adsorbed to the same extent. Apart from this, it has been shown many times from cataphoretic experiments that coagulation does *not* commence when the mobility of the micelles in the electric field is zero, but rather when it is 80 - 50% of its original value; and this means that when coagulation begins the colloidal particles still have an appreciable charge. An attempt has also been made to explain flocculation on the assumption that it is the electrokinetic potential (see p. 365), rather than the electrochemical interfacial potential, which is zero, or passes through a minimum, when coagulation begins but this view has also experienced little success.

Thus, even although it has been proved in serveral cases that foreign ions do affect the interfacial potential and that their adsorption is responsible for the changes of charge on the surface, the adsorption theory is still incapable of a general explanation of flocculation. It is particularly weak in cases where it is not easy to accept the existence of specific adsorption (which normally only occurs in the presence of capillary-active ions) on the micelles, so that their charge would be expected to remain unaffected by the addition of electrolyte.

In this most general case, the mechanism of flocculation can be understood on the basis of the interfacial potential between colloid particle and solution, if the concept of the structure of the double layer at the colloid particle-solution interface is extended, in a similar way to STERN's development of HELMHOLTZ's theory of the electrode-solution double layer (see p. 863). It is now considered that the ions which compensate for the charge of the

solid phase are present in an "atmosphere" of finite thickness comparable with the ionic cloud of the DEBYE-HÜCKEL theory (p. 175). The interfacial potential difference is therefore distributed over a certain distance from the solid phase into the solution and the charge distribution within this layer, *i.e.* the thickness of the ionic atmosphere, is dependent both on the charge on the solid phase and on the concentration of foreign ions in the solution. Consequently, if, in the absence of specific adsorption, the charge on the particles does not change on the addition of electrolyte, the charge distribution in the ionic atmosphere can ⁕be expressed as a function of the concentration of added electrolyte by means of the DEBYE-HÜCKEL theory [1].

Qualitatively the phenomena of electrolyte flocculation can be understood on this model in the following manner. As has been seen on p. 173, for a given solvent at a given temperature, the radius of the ionic atmosphere should become smaller the higher the ionic strength, *i.e.* the greater the interionic attraction. At a given molar concentration the ionic atmosphere becomes smaller the higher the valency of the ions. An ionic atmosphere of small thickness signifies an appreciable compensation of the original charges on the micelle, so that the mutual electrostatic repulsion, which controls the stability of the sol, disappears at small distances. At a sufficiently high ionic strength, therefore, the VAN DER WAALS attractive forces overcome the repulsive electrostatic forces, and consequently coagulation occurs more readily with ions of high valency. Ions of charge opposite to that on the micelles are present in the ionic atmosphere and it becomes clear that coagulation depends mainly on the valency of these ions of opposite charge. It also follows on the same view that ions charged similarly to the micelles exert a small effect on the threshold concentration for flocculation, as is actually observed, owing to their effect on the ionic strength of the solution.

Quantitatively the theory yields the general dependence of flocculation on the valency of the gegenions without additional hypotheses [2], but considerable disagreement between theory and

[1] The thermodynamic properties of double layers discussed in this section are treated by S. LEVINE, *Phil. Mag.*, 1950, [vii], 41, 53.
[2] See W. H. MÜLLER, *Koll. Beihefte*, 1928, 26, 257.

experiment occurs in some solutions. However, this disagreement
is to be expected, for the adsorption of capillary-active foreign
ions and the resultant changes in charge on the micelles must also
play some part in flocculation apart from the ionic atmosphere
effects which predominate in the absence of adsorption. It has been
shown empirically that in many cases coagulation begins for a given
sol concentration at approximately the same value of the individual
activity coefficient of the gegenions, calculated from the DEBYE-
HÜCKEL theory [1]. The repeatedly observed dependence of the
threshold concentrations for flocculation on the concentration of
the sol (BURTON's rule) has not yet been completely clarified,
but is probably also due partly to adsorption effects.

Bibliography: A. S. C. LAWRENCE, *Colloids*, *Annual Reports*, *Chem. Soc.*,
London, 1940, 90; E. J. W. VERWEY and J. TH. G. OVERBEEK, *Theory of Stability
of Hydrophobic Colloids*, Amsterdam, 1948; J. A. V. BUTLER *et al.*, *Electrical
Phenomena at Interfaces in Chemistry, Physics and Biology*, London, 1951.

3. Electrokinetic Phenomena

Up to now, interfacial phenomena for static systems, where
the two phases are at rest relative to each other, have been
discussed. If one of the phases is moved relative to the other a
number of characteristic electrokinetic phenomena can be ob-
served which have gained importance both in practical and theo-
retical electrochemistry. The following closely interconnected
effects have been observed:

(a) Colloids suspended in a medium, migrate in an electric
field to cathode or anode according to the sign of their charge.
This is termed "cataphoresis" or "electrophoresis".

(b) If the solid phase is fixed and porous, and is permeable
to the liquid phase, the liquid moves relative to the solid phase
in an electric field. This is termed "electroendosmosis".

(c) The converse of electroendosmosis occurs when a liquid is
forced through a porous plug. The potential difference set up at
the plug is termed the "streaming potential".

(d) The converse of cataphoresis is the electrophoretic potential

[1] Wo. OSTWALD, *Koll. Z.*, 1939, **88**, 1; 1941, **94**, 169.

which is observed when particles suspended in a liquid move under the influence of gravity. This is termed the "sedimentation potential", or "DORN Effect".

The first three effects are of practical importance, and are particularly useful in the study of the electrical double layer at interfaces such as glass-liquid or quartz-liquid.

(i) *Electrophoresis*

Colloidal solutions may be regarded as electrolytic solutions in which one of the ionic species consists of very large ions each carrying a correspondingly large charge, and consequently the laws of ionic migration can be applied to the movement of colloidal particles in an electric field. From (I, 55) the mobility, *i.e.* the velocity under unit potential gradient, of a spherical particle with charge $z_i e_0$ is

$$u_i = \frac{z_i e_0}{300\,P} \frac{\text{cm./sec.}}{\text{volt/cm.}}$$

at infinite dilution. Here P is the hydrodynamic frictional force on the moving particle and is expressed from STOKES's law in terms of the viscosity η of the solvent and the radius r of the particle. At finite concentration the particle is retarded additionally in two ways by the interionic attraction, *viz.*, by the electrophoretic and relaxation effects (p. 180), which arise from the ionic atmosphere surrounding the colloid particles (see p. 380).

Now according to the theory of flocculation discussed above, each colloid particle carries a double layer which extends into the solution to a distance dependent on the ionic concentration present. To maintain electrical neutrality the total charge $z_i e_0$ on the colloid particle is the same as the net charge on the "ionic atmosphere", as in the analogous case of ions. During the migration of the colloid particle under the influence of the electric field a certain amount of liquid is dragged along with it and forms a layer of thickness δ usually less than the thickness of the diffuse double layer. An "effective charge" Δe can thus be ascribed to the particle and this is given by the charge on the particle itself dimished by the charge on that part of the ionic atmosphere

which is within the distance δ (*i.e.* up to the end of the water sheath which is dragged along by the particle). Δe is thus equal and opposite to the charge on the remainder of the ionic atmosphere beyond the distance δ. It can be seen that Δe is hence much smaller than the actual charge $z_i e_0$ on the micelle, and must depend upon the thickness of the diffuse double layer compared with δ. It consequently depends upon the ionic concentration in the solution. This is so because, as seen in the previous section, the thickness of the double layer depends upon the concentration of electrolyte in the solution. That part of the diffuse double layer outside the distance δ may be considered to be "sheared off" the particle, *i.e.* not effectively to accompany it during migration, so that Δe is the charge which is analogous to $z_i e_0$ in the case of electrolytic conduction. The relation for the mobility of the particles becomes, in place of (I, 55),

$$u_i = \frac{\Delta e}{300 \cdot 6\pi\eta\,(r_i + \delta)} = \frac{\Delta e}{300 \cdot 6\pi\eta\,a_i}\,, \tag{44}$$

where STOKES's Law has been used to substitute for P, and $a_i\,(= r_i + \delta)$ is the net radius of the particle, including its attendant water sheath; u_i is then dependent on the ionic concentration of solution because δ depends on the concentration. It is usual to the introduce the electrokinetic potential ζ of the moving particle. The substitution is carried out in the following way. The particle of radius a_i is treated as a spherical condenser the capacity of which is given by

$$C = \frac{300 \cdot \Delta e}{\zeta}\,, \tag{45}$$

where Δe is expressed in electrostatic units and ζ in volts (see p. 611); also, the capacity of a spherical condenser of radius a_i in a medium of dielectric constant ε is $a_i\varepsilon$, so that elimination of C leads to the equation

$$\Delta e = \frac{\zeta\varepsilon a_i}{300}\,. \tag{46}$$

Substituting for Δe in (44) gives

$$u_i = \frac{\zeta\varepsilon}{300^2 \cdot 6\pi\eta} \tag{47}$$

The mobility of the particle is thus a function of the electro-kinetic potential. Further, owing to the fact that the dimensions of the diffuse double layer and hence also the electrokinetic potential, depend on concentration (see p. 880), it also depends upon the interionic forces in solution [1].

The second retarding influence, the relaxation effect, originates from the fact that the micelle moves through its own double layer which is continuously being broken down behind the micelle and built up in front of it (see p. 180). The resulting lack of symmetry of the double layer causes a retarding force to be exerted in a direction opposite to the motion of the micelles. However, the application of the DEBYE-HÜCKEL-ONSAGER theory of relaxation effects to colloidal solutions is difficult because in the theory for ionic solutions it is assumed that the size of the central ion is small compared with that of the ionic atmosphere. This is, of course, not true for ionic micelles. The expressions derived by use of the DEBYE-HÜCKEL-ONSAGER theory are therefore only applicable for very dilute solutions of colloids, where the radius of the ionic atmosphere, $1/\varkappa$, is great, i.e. the expression representing $\varkappa \cdot a$ in (V, 49) is small. There is clearly little possibility of applying the theory to colloids in concentration regions of practical interest. A more recent derivation of the retardation effects in colloidal solutions [2] taking into account the interaction between the relaxation and electrophoretic effects leads to an equation for the mobility u_i which is similar to (47) but incorporates a series of correction terms. These terms are functions of $\varkappa \cdot a$, i.e. they depend on the dimensions of the diffuse double layer and on ζ, and they differ for symmetrical and asymmetrical electrolytes. Equation (47) then becomes

$$u_i = \frac{\zeta \varepsilon}{300^2 \, 6 \, \pi \, \eta} \cdot f(\varkappa a, \zeta) \, . \tag{47a}$$

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[1] The values of u_i are of the same order as the mobilities of ordinary ions. They have the value 3 to $5 \cdot 10^{-4}$ cm./sec. at room temperature (see p. 205). If this value is introduced into equation (47), there is obtained the following expression:

$$\zeta = \frac{6 \cdot 3 \cdot 14 \cdot 0 \cdot 01 \cdot 300^2 \cdot 3 \cdot 10^{-4}}{80} \cong 0 \cdot 07 \text{ volt.}$$

Electrokinetic potentials are hence very small; this is because the charge on the micelles is largely negated by the gegenions from the double layer.

[2] J. Th. G. OVERBEEK, Koll. Beih., 1943, 54, 287.

The correction term $f(\varkappa a, \zeta)$ has been calculated for various values of ζ and $\varkappa \cdot a$ and is given in tables. At comparatively large ζ potentials particularly ($\zeta > 25$ mV), the relaxation effect has a marked influence on the mobility of the micelles. If the mobility u_i is studied as a function of the electrolytic concentration of the solution, complex curves with maxima and minima are obtained. The shape of the curves is due to the superposition of two effects, firstly the change of ζ and secondly, the change of the correction term $f(\varkappa a, \zeta)$ with concentration of added electrolyte. At sufficiently high ionic concentrations, especially in the presence of polyvalent ions, u_i decreases with increasing concentration as if the double layer were undergoing contraction. Fig. 57 shows this in the dependence of the mobility of the particles in a silver iodide sol on the concentration of various ions of opposite sign. The above theoretical relation is clearly no longer valid when adsorption of the ions of the added electrolyte on the colloidal particles takes place and in these circum-stances the experimentally obtained relation between u and ζ often lacks a full theoretical explanation.

The practical *determination of the mobility of colloidal particles* can be carried out macroscopically by the moving boundary method, as described on p. 572. The suspension is covered by a suitable liquid and the displacement of the boundary under the applied field is followed by Töpler's Schlieren method. Alternatively a microscopic method is used, where the migration of an individual particle is followed. Both methods have been developed in recent years and have yielded results of high precision (see Chapter XIII, p. 592 for experimental details).

Fig. 57. Mobility of a silver iodide sol as a function of the concentration of various gegenions

The *practical significance* of macroscopic electrophoretic experiments, besides their use in the determination of the ζ potential, lies in their application to the separation of colloids from one another, utilising their different electrophoretic mobilities. Electrophoresis is being used increasingly as a *method of purifi-*

cation of colloids and possesses the advantage of applying only mild conditions, in contrast with chemical methods, so that even labile proteins, for example, can be obtained in a pure condition in this way. The mobility can be used to characterise pure proteins, for the "mobility curves" (plots of u as a function of pH) show that u changes from positive to negative according to the charge on the ampholyte. At the isoelectric point the mobility is zero (see p. 824), and the slope of the mobility curve in the neighbourhood of the isoelectric point can also be used for the identification of certain proteins.

A modern type of electrophoresis apparatus as used in the separation of proteins is shown diagrammatically in Fig. 58. The colloidal solution is placed in a U-tube, with compartments which can be effectively joined to or separated from each other, for analysis of their contents, by means of air pressure. The upper part of the U-tube and the large vessels intended for the Ag-AgCl electrodes [1] are filled with a buffer solution of conductance approximately the same [2] as that of the colloidal solution and with which a boundary with the latter is made. The large vessel prevents the products of electrolysis from reaching the colloidal solution. By suitable design of the cross-section of the tube, the heat exchange with the surrounding thermostat is improved. It is the practice to work at 4 °C. (*i.e.* at the density maximum for aqueous solutions, where the change of density with temperature is very small). In this way convection currents, which spoil the sharpness of the solution boundary, are almost eliminated. Using these and other devices it is possible for example to separate the various proteins of blood serum quantitatively and in a pure state.
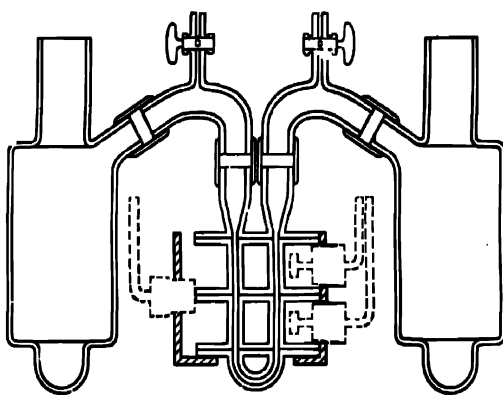
Fig. 58.

Cataphoresis apparatus according to TISELIUS

For the *measurement of ζ potentials* the microscopic method is more suitable, if the individual particles of a colloidal solution are visible under the microscope. The migration of the particles under the field of vision is directly observed and measured in a capillary cell using a travelling microscope. Account must be taken of the fact that the measured (apparent) velocities of the particles depend

[1] The Ag-AgCl electrode is used because when it functions as an anode the deposited chlorine forms AgCl and when as a cathode the AgCl is reduced to Ag with the formation of HCl. Thus in neither case are bubbles produced which would disturb the boundary.

[2] The conductance of this solution should be approximately the same as that of the colloidal solution so that no differential heating effects occur on passage of a current.

on the distance of the particles from the wall of the cell. The apparent velocity is composed additively of the actual velocity, u_e, and the velocity u_0 of the liquid due to electro-endosmosis (see p. 388). The dependence of the streaming velocity u_0 of the liquid on the radius R of, say, a cylindrical cell, may be calculated if the cell is closed from outside so that the liquid streams in one direction at the walls of the cell, but in the opposite direction in the middle of the tube. Considering the case where the particles are negatively charged, then if motion towards the anode is taken as positive, the colloidal particles near the wall of the cell will have an apparent velocity $u_e + u_0$, whilst those in the centre of the tube will apparently move with a velocity $u_e - u_0$. It is found[1] that only at distances of $0.293 \ R$ and $1.707 \ R$ (where R is the radius of the tube) will the apparent velocity be the same as the real one. Thus, in a plane passing perpendicularly through the axis of the cell there is a parabolic distribution of velocities as shown in Fig. 59. The experimental points for the experiment illustrated in Fig. 59 are derived from observations on oil emulsions and agree with the calculated curves within the limits of error of the method. It is clear, then, that the true mobilities of the colloid particles can be obtained from measurements of the apparent velocity at known distances from the wall of the cell. Agreement of the microscopic with the macroscopic method is good.
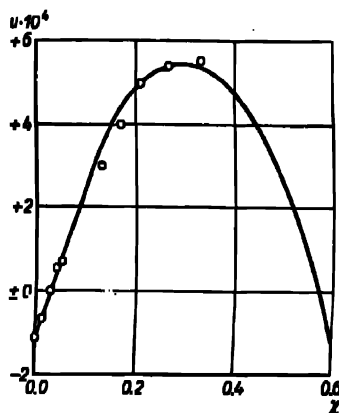
Fig. 59. The effect of electroendosmosis upon the mobility of colloids in electric fields

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[1] Let the radius distance from the centre of the tube to a given point in the liquid be r and the radius of the tube be R. The total transport of liquid per second through the tube is $\int_0^R V_r \, 2\pi r \, dr$, where V_r is the velocity of transport at a point r. This integral is clearly zero for a closed tube. The distribution of velocities in such a case is given [*] by $V_r = c_1 (r^2 - c_2)$, where c_1 and c_2 are constant. Hence, $\int_0^R c_1 (r^2 - c_2) \, 2\pi r \, dr = 0$, and $c_2 = R^2/2$. Therefore, $V_r = c_1 (r^2 - R^2/2)$. When $V_r = 0$, the velocity of the particles is their own true velocity and the distance at which this occurs is hence at $r = R/\sqrt{2} = 0.707 \ R$. Hence, measuring from the wall of a tube, the distances at which the electrophoretic velocity will be the real velocity are

$$(1 - 0.707) \ R = 0.293 \ R \quad \text{and} \quad (1 + 0.707) \ R = 1.707 \ R \ .$$

[*] S. MATTSON, *J. Phys. Chem.*, 1933, **37**, 223.

(ii) *Electroendosmosis*

Electroendosmosis is one of the earliest known electrochemical phenomena, and it was discovered shortly after the decomposition of water by an electric current had been recognised. Fig. 60 shows diagrammatically an apparatus for the measurement of electro-osmotic pressure. In this figure, D is a diaphragm permeable to the liquid. When a potential difference is applied between the electrodes the liquid migrates in a direction characteristic of the nature of the diaphragm and of the liquid. Migration causes the meniscus in the capillary K to be displaced and the hydrostatic pressure thus produced leads to the establishment of a stationary state, because a tendency to stream back arises in the liquid due to this pressure. The direction of streaming in electroendosmosis may be decided by applying an empirical rule whereby the phase with the higher dielectric constant is positively charged with respect to the other phase. On account of the high dielectric constant of water aqueous solutions usually migrate towards the cathode and the walls of the diaphragm become negatively charged.

Fig. 60. Apparatus for the measuremnet of the electro-enodsmotic pressure (schematic)

Electroendosmosis is fundamentally the same as electrophoresis, but differs in that the solid particles form a porous, immobile aggregate and cannot thus themselves migrate under an applied potential difference. The distinction may be appreciated by considering the diaphragm replaced by a single cylindrical capillary of radius r (see Fig. 61). Let it be again assumed that a HELMHOLTZ double layer exists at the surface of the solid phase, and that the liquid side of this is somewhat diffuse, due to the thermal energy of the liquid which also influences the dimensions of the ionic atmosphere. Let it further be assumed as before that a fixed liquid layer exists on the wall of the

capillary and that this extends out into the solution to a distance
less than the thickness of the total double layer. It follows that

an excess
charge Δe
must be as-
cribed to
the solution
and this in-
teracts with
the electric
field causing
the liquid to
move. The
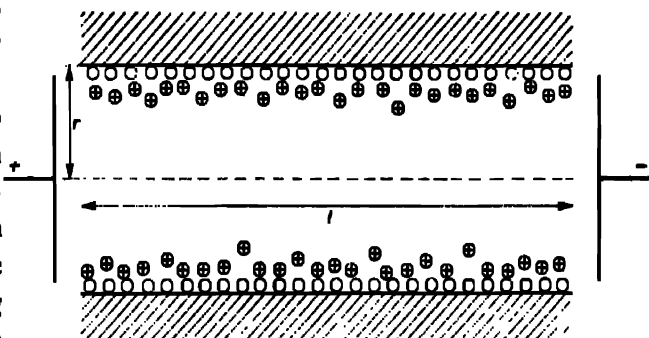
Fig. 61. Development of electroendosmotic pressure

excess charge on the solution gives rise to an electrokinetic po-
tential between the solid phase with its attached liquid layer and
the bulk of the solution. This potential difference is related to
the velocity of electroendosmosis by an equation similar to (47),
which can be deduced from considerations analogous to those
on p. 383 [1], and is

$$u_0 = \frac{\zeta \, \varepsilon}{300^2 \cdot 4 \pi \eta} \, . \tag{48}$$

Here u_0 denotes the streaming velocity at a field strength of
1 volt/cm. The amount of liquid streaming through the capillary
in unit time then follows as

$$\frac{dV}{dt} = \pi r^2 \cdot u_0 \cdot E = \frac{r^2 \zeta \, \varepsilon}{300^2 \cdot 4 \eta} \cdot E \, , \tag{49}$$

where ζ is in volts, and E is the applied potential difference.

This equation applies when the streaming liquid can escape
without setting up a hydrostatic pressure. In the case of the
arrangement shown in Fig. 60, where a stationary state is set
up, liquid flows along the walls of the capillary in one direction
and returns through the centre of the tube owing to the hydro-
static pressure set up [2]. For laminar streaming, using POISEUILLE's

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[1] If the electrophoresis is of cylindrical and not spherical particles, the denomi-
nator of (47) contains the factor 6 instead of 4, and the equations for electro-
endosmosis and electrophoresis become identical.

[2] As in the microscopic method for electrophoresis there is also a stationary layer
here. It can be shown to lie at $R/\sqrt{2}$ from the axis of the capillary.

law, it follows that the rate of backward streaming through the tube is

$$\frac{dV'}{dt} = \frac{\Delta p \cdot \pi r^4}{8 \eta l} \ , \tag{50}$$

where l is the length of the capillary.

In the stationary state $\dfrac{dV}{dt} = \dfrac{dV'}{dt}$ and hence,

$$\frac{r^2 \zeta \varepsilon \cdot E}{800^2 \, 4 \eta} = \frac{\Delta p \cdot \pi r^4}{8 \eta l} \ . \tag{51}$$

From this, the electro-osmotic pressure follows as:

$$\Delta p = \frac{2 \zeta \varepsilon l}{800^2 \, \pi r^2} \cdot E \ . \tag{52}$$

The electro-osmotic pressure should thus be inversely proportional to the square of the radius of the capillary and this is approximately confirmed by measurements with glass capillary tubes. The electrokinetic potential can also be obtained from measurements of Δp, as all the other terms in (52) can be determined. This potential is of course affected by addition of electrolyte to the liquid in the capillaries, *i.e.* by alteration in the thickness of the diffuse double layer at the surface of the solid phase. Here again, however, the phenomena become unclear, owing to ionic adsorption effects.

Besides the use of electrophoresis for the *separation of proteins in the pure state*, mentioned above, both electrophoresis and electroendosmosis are of considerable practical and some technical importance. Their importance in these respects lies mainly in their use for the purification and deposition of certain materials which carry charges of like sign in the colloidal state, and can therefore be separated by electrophoresis from uncharged or oppositely charged impurities. This principle is used in the *electrophoretic purification* of clay and kaolin. The clay is made into a sludge with water and acquires a negative charge which is increased by the addition of small quantities of alkali (containing potential-determining OH' ions). The suspension forms a stable colloid while impurities are deposited. By then subjecting the suspension to electrophoresis the colloidal particles are deposited on a rotating metal cylinder functioning as anode and are thus continuously removed. At the same time dehydration of the clay occurs. Other processes carried out in a similar way are the electrophoretic dehydration of peat, the deposition of crude rubber from rubber latex and the purification of lime and gelatin, *etc.*

In many cases it is possible to *deposit colloids on metal electrodes* so that adherent deposits are formed. For example, using a solvent mixture such as acetone-water as dispersion medium, rubber or graphite coatings can be produced. Filaments for use in valves, *etc.*, are also obtained in this way by depositing colloidal suspensions of alkaline earth metal carbonates on an electrode.

Special *electro-osmotic techniques* are also used for dehydration, using suitable diaphragms charged in the appropriate sense relative to the solution. Since the flow of liquid per unit time increases with field strength, high applied potentials are used and the electrokinetic potential at the diaphragm is made as large as possible by the addition of small quantities of electrolyte (usually containing H_3O^+ and OH^- ions). In this way pure silicic acid can be prepared from waterglass solutions, and pure alumina from a solution of an aluminate. The waterglass solution is placed in the anode compartment of the electrolysis cell which has an alumina diaphragm. Electrolysis is first carried out at a low potential when the alkalis migrate towards the cathode compartment. As this process continues the potential difference across the cell rises as the conductance of the solution decreases, and electroendosmosis starts to take place. Since the alumina diaphragm is negative relative to the solution, liquid is transferred from anode to cathode compartments, and finally, a very concentrated silicic acid solution remains. By using a positively charged diaphragm any other acids present may be subsequently removed, in which case the solution is placed in the cathode compartment of the cell. The migration of the foreign anion into the anode compartment is then assisted by the electroendosmotic transport of water which streams towards the anode. Most diaphragms used in these experiments are negative with respect to the solution, but positive diaphragms may be made of MnO_2, PbO_2, and similar oxides.

The *electrophoresis of gaseous colloids* (aerosols) also has considerable technical importance. Solids or liquids highly dispersed in the form of smokes or fogs are often extremely stable and thus difficult to break down. The electrical charge on the particles in aerosols does not play the same essential part in determining the stability as it does, for example, in hydrosols. The charges are usually small, whilst positive, negative, and uncharged particles all occur together. Indeed, it is difficult to prepare aerosols of similarly charged particles [1], for the charges on the particles usually depend on the condensation or attachment of molecules to ions already present (condensation nuclei) or upon a subsequent adsorption of these ions. Ions can also be produced mechanically by friction, and thereby large electrical charges can accumulate and give rise to dust explosions. Accumulations of charge can also arise through the break-up of larger drops of liquid (ballo- or waterfall electricity).

To obtain rapid migration and deposition of aerosols the number of charged particles should be increased, and this condition may be achieved by a point discharge on a cathode to which is attached a thin wire emitter electrode surrounded by a cylindrical anode. A strong field (several thousand volts) is applied so that the cathode emits electrons which ionise the gas molecules by impact (see Chapter XII). The gaseous ions then act as condensation or attractive nuclei for the

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[1] Such aerosols do, however, occur in natural fogs and in storm clouds, and show an unusual stability owing to mutual repulsion between the charged particles.

colloidal particles and migrate with their attached particles to the electrodes where they are deposited. Uncharged particles also move because they become polarised in the strong non-homogeneous field. The induced dipoles not only experience a turning movement, as in a homogenous field, but are also subjected to a force which removes them to positions of higher field strength. Before the electrodes are reached dipole interaction causes a polar attachment of the particles to each other (see p. 105). Long threads of particles then arise which increase slowly in dipole moment, thereby inducing a greater acceleration towards the (smaller) electrode where the field strength has increased. In the electrical condensation of smokes, *etc.*, it is hence the polarisability as well as the charge on the colloidal particles which is important.

(iii) *Streaming Potentials*

If the process of electrophoresis is reversed and the liquid is forced through a capillary a potential difference called the *streaming potential* arises between the ends of the capillary. The potential difference can be measured by using two normal electrodes connected to the liquid in the capillary by means of a siphon tube containing agar-agar solution with KCl present. The origin of the streaming potential may be pictured as follows. It has been seen that one part of the double layer remains firmly attached to the surface of the solid phase while the remainder is diffuse in the sense of an ionic atmosphere (*cf.* STERN's theory, p. 368). When liquid streams over the surface of the solid phase, ions of the same sign in the diffuse part of the double layer are swept away and the ends of the capillary become oppositely charged. The streaming potential thus set up causes ionic migration and a stationary state is eventually reached. The magnitude of the potential difference $\Delta\psi$ must also depend on the conductance of the solution. At equilibrium the amount of current i' carried by the streaming liquid must be equal to that carried by the countercurrent of ions. The latter ionic current i can be found by applying OHM's law and is

$$i = \frac{\Delta\psi}{R} = \Delta\psi\varkappa\frac{\pi r^2}{l} \;,$$

where $\varkappa$ is the specific conductance of the liquid, and r and l are the radius and length respectively of the capillary; i' is found by multiplying the excess charge Δe of the streaming liquid

compared with that of the immobile liquid layer (see p. 882) by the velocity V of the streaming liquid. Since i' depends on Δe, it varies with the electrokinetic potential ζ, in addition to varying with the applied pressure P which forces the liquid through the capillary. It can easily be shown that

$$i' = \frac{\zeta \varepsilon r^2}{4 l \eta} \cdot P \; .$$

The equilibrium condition $i = i'$ then leads to the following expression for the streaming potential:

$$\Delta \psi = \frac{\zeta \varepsilon \cdot P}{4 \pi \eta \cdot \varkappa} \; . \tag{58}$$

It thus appears that the streaming potential should be directly proportional to pressure and inversely proportional to the specific conductance of the liquid provided laminar flow exists. The equation complies with the facts fairly well, but discrepancies observed at low pressures indicate its approximate nature [1].

B i b l i o g r a p h y : ABRAMSON, MOYER and GORIN, *Electrophoresis of Proteins*, Reinhold, 1942; L. G. LONGSWORTH, *Review of the Technique and Theory of the Electrochemistry of Proteins*, Ann. New York Acad. Sci., 1945, 46, 211; F. BOOTH, Theory of Elektrokinetic Effects, *Nature*, 1948, 161, 83; J. A. V. BUTLER et al., *Electrical Properties of Interfaces in Chemistry, Physics and Biology*, London, 1951.

[1] Fore more exact relations, see S. M. NEALE, *Trans. Faraday Soc.*, 1946, 42, 473.

IRREVERSIBLE ELECTRODE PROCESSES

The greater part of the preceding material in this book has dealt with phenomena taking place in the bulk of the solution. In Chapters VII and VIII electrode potentials and galvanic cells were discussed as far as thermodynamically reversible processes are concerned. The property of reversibility made it possible to discuss these processes in terms of thermodynamic theory without reference to the detailed mechanism of the processes taking place at the electrode-solution interface. No net current flows across the interface between a reversible electrode and the solution. The majority of electrode processes (*e.g.* those taking place in electrolysis), however, involve the passage of a net current across the electrode-solution interface. These processes take place at a finite speed. They are spontaneous, *i.e.* thermodynamically irreversible, and cannot therefore be treated directly by thermodynamic methods.

A considerable section of electrochemistry is concerned with irreversible electrode processes, the mechanism of which will be studied partly upon the basis of the knowledge of the electrical double layer (Chapter X).

1. Definition and Measurement

When a current flows across an electrode-solution interface it is normally found that the electrode potential changes from the reversible value it possesses before the passage of current. In a galvanic cell, passage of a current would cause the potentials of both electrodes in the cell to change from their reversible values, so that the e.m.f. of the cell would be different upon passage of current from the reversible e.m.f. measured when a counter e.m.f.

is applied to the cell in such a way that no net current flows. The departure of the e.m.f. of a cell, or of an electrode potential, from its reversible value upon passage of a current, and phenomena directly connected with this departure, are called *"polarisation"* [1], and the electrodes or cells are said to be polarised.

A more specific term of similar meaning to that of polarisation, is *overpotential* (or *overvoltage*). The overpotential of an electrode is the difference in potential between an electrode across which passes a certain current density (c.d.) and a reversible electrode in the same solution. The overpotential of an electrode at a current density of i is represented by η_i, *i.e.*,

$$\eta_i = e_i - e_r \, , \qquad (1)$$

where e_i is the electrode potential whilst current at i amps. per sq.cm. is passing across the electrode-solution interface.

Various types of overpotential may be distinguished. Thus, in some electrode processes a film of oxide or some other substance forms on the electrode surface and sets up a resistance to the passage of current across it. If the current strength is I and the resistance of the electrode surface is R ohms, this *ohmic overpotential* is then given by IR. The ohmic overpotential at an electrode can reach considerable values, *e.g.* several hundred volts. What may be termed an ohmic pseudo-overpotential is also observed when the LUGGIN capillary tip (see p. 399), used in measuring the potential of the electrode, is at an appreciable distance from the electrode surface; [2] an ohmic pseudo-overpo-

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[1] This term should not be confused with one of the same name in dielectric theory. Strictly, use of the term polarisation should be preceded by "electrolytic" or "dielectric", according to the case in point.

[2] Let R be the resistance between the electrode (considered here as a plane surface) and the equipotential surface of area A equal to that of the electrode, and in which the capillary tip is situated. Let the cross sectional area of the tip of the LUGGIN capillary be dA and the resistance of the column of electrolyte between it and the electrode be dR. If the current strength is I, the current flowing through the electrode-capillary column is $I \dfrac{dA}{A}$ (or dI). The resistance of the column is correspondingly $R \dfrac{A}{dA}$ (or dR). The ohmic pseudo-overpotential is $dIdR$, *i.e.* IR. It depends, therefore, upon the current density, electrode area and distance from the electrode of the capillary tip, but it is independent of the radius of the latter.

tential is then included in the true overpotential of the electrode solution interface, owing to the passage of current through the section of electrolyte between the cathode tip and the electrode surface.

This pseudo-overpotential only becomes appreciable at high current densities or low concentrations. At very high current densities (e.g. $i > 10$ amp. per sq.cm.) even in concentrated solution (e.g. $5N$ aqueous HCl) it is considerably larger than the true overpotential of the electrode and has to be eliminated by a special method of measurement (see p. 400). The total ohmic overpotential is represented by η_0.

A second type of overpotential is caused by the existence of a difference in concentration of the ions between the electrode-solution interface and the bulk of the solution. Thus, suppose a silver electrode is placed in an aqueous solution of silver nitrate of concentration c_b and polarised at a current density of i amps per sq.cm., then the concentration of ions at the electrode-solution interface, c_e, will be less (assuming the process to be a cathodic one, i.e. to involve deposition) than that in the bulk of the solution. The potential of the working electrode (i.e. the one across which a current is being passed) hence depends upon c_e while that of the corresponding reversible reference electrode, against which the potential of the working electrode is measured in the determination of its overpotential, depends upon c_b. There is thus a difference between the potentials of the working and reversible electrodes. This type of overpotential is termed "concentration overpotential". It forms the basis of polarography and polarographic analysis.

The third type of overpotential is concerned with the reaction occurring upon electrolytic deposition of ions or evolution of gases. In most electrode processes it is found that after making allowance for the ohmic and concentration overpotentials, the electrode still exhibits some overpotential, which is particularly marked, for example, in the evolution of hydrogen and oxygen. This overpotential is connected with the energy of activation of the rate controlling reaction in the process of transferring the solvated ions on the solution side of the double layer to the final state either in the metal surface or as evolved gas. This rate controlling process is affected by the potential of the electrode and can only occur at appreciable speeds if the electrode potential is displaced from

the reversible value towards more negative values for cathodic processes and more positive values for anodic processes. As the increase in the velocity of the rate controlling process brought about by the electrode potential is equivalent to that which would be caused by a reduction in the activation energy of the process, this type of overpotential is termed *activation overpotential*, η_A . [1,2]

[1] Activation overpotential as here defined is sometimes divided into two sub-groups. The first is termed 'transition overpotential' which is activation overpotential in those cases where the rate controlling process is that of passage over an energy barrier between the solution and the electrode, e.g. the evolution of hydrogen from aqueous acid solutions which at some electrodes is controlled by the rate of discharge of protons adsorbed in the HELMHOLTZ section of the double layer at the electrode-solution interface. The second sub-group of activation overpotential is termed 'reaction (or chemical) overpotential', by which is meant activation overpotential in those cases where the rate controlling step is a chemical reaction, e.g. the combination of two hydrogen atoms to form a hydrogen molecule. These subdivisions are not at present of great use, however, because they require knowledge of the rate controlling step in the process before the type of overpotential can be named, and this is in some cases as yet speculative.

[2] *Note on Decomposition Voltage.*

When the applied potential difference across two electrodes in, e.g., an aqueous solution of sulphuric acid, is increased the potential-current relation is as shown in Figure 62. The applied potential difference corresponding to the point of sudden inflection is termed the *decomposition voltage* of the substance undergoing electrolysis, for it is at the corresponding applied potential that free deposition of ions from the electrolyte commences, i.e. that the electrolyte begins to undergo decomposition at an appreciable rate. Suppose that the electrodes in the system behave as ideal reversible electrodes. Then, the decomposition voltage represents the sum of the two reversible deposition potentials of the ions being deposited. The cell reaction consists in the decomposition of the electrolyte, and hence the free energy change in this process must be
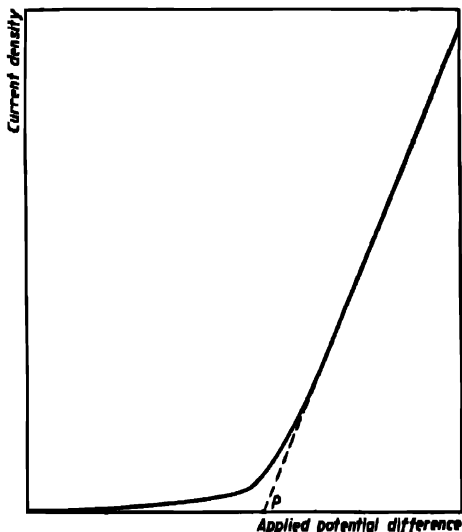
Fig. 62. The relation between current density through a cell and the applied potential difference. P corresponds to the "decomposition voltage"

The overpotential, η, observed at an electrode under given conditions is defined by the sum of the three types of overpotential described above, i.e.,

$$\eta = \eta_0 + \eta_\sigma + \eta_A. \qquad (2)$$

To examine the ohmic, concentration or activation overpotential separately it is necessary to reduce the other types of overpotential to negligible values. True ohmic overpotential can generally be recognised easily, since it is usually very much larger (particularly at higher current densities) than the other types of overpotential. Concentration overpotential can be studied if the absence of resistive films upon the electrode is ensured and an electrode is chosen at

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given from (VII, 5) by $-n_s F E_s$. This expression is sometimes of use in obtaining the free energy of formation of, for example, oxides or sulphides of metallurgical importance, where the decomposition voltage obtained upon electrolysis is sufficiently free from irreversible components and thus gives an approximate value of $-\Delta G$. [1]

More usually, considerable (activation and concentration) overpotential arises at the electrodes during the measurement of a decomposition voltage. Further, as the applied potential *between the electrodes* is measured, an ohmic pseudo-overpotential dependent upon the dimensions and concentration of the electrolyte between the electrodes, the specific resistance of the electrolyte and the current strength is also included. The value of the decomposition voltage could thus in general be represented by

$$E_d = e_{AA'} - e_{BB'} + \Sigma\eta + IR,$$

where $e_{AA'}$ and $e_{BB'}$ are the reversible deposition potentials of the ions A and B at the electrodes A' and B', $\Sigma\eta$ represents the algebraic sum of the activation and concentration overpotentials at both electrodes at the current density of the point of sudden inflection, I represents the current strength and R the resistance between the electrodes. In the *general case*, therefore, decomposition voltage depends also upon irreversible processes, so that the free energy of the cell reaction (see above) is not always derivable from it. In practice it seldom leads to information of value equal to that obtained from measurements of the potentials of single electrodes at various current densities, and it has no simple physical significance.

Fig. 62 shows the existence of a small current which flows before the decomposition voltage, and which disobeys OHM's Law. This current depends upon a small but appreciable rate of deposition of ions *before* the actual reversible deposition potential has been reached and upon the fact that current is used in making up for electromotive substances near the electrode which diffuse away with time. Both the deposition rate and the rate of loss by diffusion increase with increasing potential, in accordance with the facts illustrated in Fig. 62.

[1] H. J. T. ELLINGHAM, *J. Soc. Chem. Ind.*, 1944, **63**, 125.

which the activation overpotential is negligible (*e.g.* a mercury electrode in an aqueous mercurous nitrate solution). The activation overpotential can be examined in the absence of resistive films, if the concentration overpotential is diminished to negligible proportions by rapid agitation of the electrolyte in the vicinity of the electrode so that the diffusion of ions to the electrode surface is increased and c_s becomes practically equal to c_b.

An immediate experimental distinction between the three types of overpotential can be made by an examination of their rates of decay with time, after the cessation of the polarising current. Ohmic overpotential decays instantaneously; concentration overpotential decays slowly following no simple law, and activation overpotential decays exponentially, with respect to time.

Overpotential can be measured in two fundamentally different ways. In the "*direct method*", the electrode under examination is connected to a reference electrode, the connecting tube being drawn out to a small diameter (LUGGIN capillary, see Fig. 68) so that when its tip is very near to the electrode no appreciable potential difference arising from the ohmic potential drop in the solution (ohmic pseudo-overpotential) is included in the observed e.m.f. of the cell (see p. 395). At higher current densities, the pseudo-ohmic overpotential becomes appreciable, even though the LUGGIN capillary tip is nearly in contact with the electrode. Under these conditions one of two alternative methods can be used for the measurement. The direct method may be modified

Fig. 68.

LUGGIN capillary in vicinity of an electrode

by making measurements on a series of LUGGIN capillaries at various distances from the electrode, where an extrapolation to zero distance between the electrode and the LUGGIN capillary gives the overpotential in the absence of an ohmic component [1]. Alternatively, the "*indirect or commutator method*" may be used to avoid the problems of the ohmic overpotential. In this a commutator is used to connect the working electrode alternately with the polarising circuit and the measuring circuit. Thus, when the potential of the

[1] A. M. AZZAM, *Thesis*, London, 1949.

electrode is actually being measured, no current is flowing between cathode and anode and therefore the ohmic overpotential is momentarily zero. The difficulty of this method is that as the measurement is made after the polarising current has ceased to flow, the recorded electrode potential tends to be less than the actual electrode potential owing to decay of the potential with time. However, if measurements are made at sufficiently short intervals after the cessation of the current, there is no significant error introduced in this way [1]. Increase of current density causes the rate of decay of the electrode potential to increase, and thus tends to increase the error of the commutator or indirect method, which hence cannot at present be used at current densities above about 1 amp./sq.cm. At higher current densities the modification of the direct method, mentioned above, must be used. The main advantage of the commutator method is in making measurements which are free from true ohmic overpotential, *i.e.*, from the ohmic resistive effects caused by films, rather than for avoiding the comparatively small ohmic pseudo-overpotentials often associated with the use of a cathode tip, in the current density range in which the commutator can be used.

2. Concentration Overpotential

(i) *The Diffusion Controlled Current at a Stationary Surface*

It has been pointed out (see p. 396) that during cathodic deposition of ions at an electrode, the activity of the ions in the vicinity of the electrode-solution interface will be less than that in the bulk of the solution. The relation between the concentration and distance from the cathode is given by the curve AB as shown in Fig. 64. For the purposes of the elementary theory, it is more convenient to consider the concentration to change linearly with the distance from the electrode and to become equal to that in the bulk at a definite point C. The distance YC is termed the *thickness of the diffusion layer*, and is represented by δ. This distance is *effectively* the thickness of the diffusion layer, which really extends from Y to B.

The comparative lack of ions in the vicinity of the electrode

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[1] A. HICKLING, *Trans. Faraday Soc.*, 1937, **33**, 1540.

induces ions to dif-
fuse towards the elec-
trode and the rate of
this flow can be cal-
culated from FICK's
diffusion equation,
according to which
the rate of diffusion
of an entity is pro-
portional to the acti-
vity gradient across
which it diffuses.
Hence the rate of
diffusion of ions to
wards the electrode
is proportional to

$$\frac{a - a_s}{\delta}$$
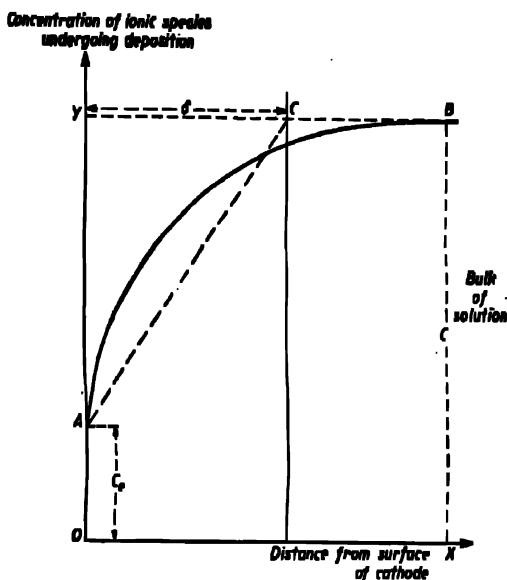
Fig. 64.

Concentration-distance relation in the vicinity of
a cathode during ionic deposition

per sq.cm. of an electrode surface, where a is the activity of the
given ionic species in the bulk of the solution, and a_s that at the
surface of the electrode. The rate is hence equal to

$$\frac{D}{\delta}(a - a_s),\qquad(3)$$

where D is a constant termed the diffusion coefficient.

In addition to the transport by diffusion, some ions are trans-
ported in a cathodic process to the electrode by means of electrolytic
transport according to FARADAY's Laws. Thus, if the current density
is i amp./sq.cm., the number of gram ions of valency z transported
in this way per second to one sq.cm. of the electrode surface is

$$\frac{n_+ i}{z F},\qquad(4)$$

as the positive ion deposited carries a fraction n_+ of the electroly-
tic current.

It follows that the total rate of transport of cations towards
the cathode is

$$\frac{D}{\delta}(a-a_s)+\frac{n_+ i}{zF}. \tag{5}$$

This must be the same as $\dfrac{i}{zF}$ and hence

$$\frac{i}{zF}(1-n_+) = \frac{D}{\delta}(a-a_s), \tag{6}$$

or,

$$i = \frac{DzF}{\delta(1-n_+)}(a-a_s). \tag{7}$$

As the current density i is increased, the value of a_s decreases. The limiting value of a_s is clearly zero and from (7) it is seen that zero value of a_s corresponds to a maximum value of the current. This maximum value of the current for the deposition of a single ionic species is termed the *limiting (or transition) current* for that species. It follows from (7) that the limiting current i_L is given by

$$i_L = \frac{DzFa}{\delta(1-n_+)}, \tag{8}$$

$$= \frac{DzFa}{\delta n}, \tag{9}$$

where n represents the sum of the transport numbers of all the ions which are not discharged at the electrode considered.

$$\therefore i_L = k\,a, \tag{10}$$

where k is a constant of meaning given by (9).

For many purposes [*e.g.* in polarography, see section (v)], it is desirable to introduce into the solution an excess of an indifferent electrolyte which carries virtually the whole of the current. In this case, $n = 1$ and hence

$$i_L = \frac{Dz_iFa_i}{\delta}, \tag{11}$$

where z_i is the valency of the ions of species i, having an activity a_i.

As i_L is the *maximum possible* rate of deposition of a given species, any attempted further increase in the current must result in a rapid shift of cathode potential from values covering the range

over which the ionic species considered above can be deposited to a range at which some other ionic species can deposit. In a system containing only one species of metal cations in aqueous solution, this other ionic species must necessarily be hydrogen. The theory of the change in potential taking place at the limiting current will be examined later (p. 407).

The above equations have been evaluated with specific reference to a simple deposition process, *e.g.* the deposition of silver ions onto a silver electrode. They apply in addition, however, to all diffusion controlled processes, so long as the steady state associated with the potential is rapidly attained. Thus, they apply to anodic processes and to oxidation-reduction processes. The latter may be either oxidation-reduction processes involving ions (*e.g.* $Fe^{\cdots} \rightarrow Fe^{\cdot\cdot}$) or those involving neutral molecules *e.g.* quinone $\rightarrow$ hydroquinone. For an oxidation-reduction process, z is the number of electrons transferred during the electrode process.

(ii) *The Diffusion Layer*

Before calculations of the limiting current for a given ionic species can be made from the equations of the last section, it is necessary to determine the value of δ, the thickness of the diffusion layer. Considering the motion of the given ionic species towards the cathode, Fick's diffusion law can be applied in the following way[1]. If the concentration gradient is dc/dx, the quantity of the species transferred per second is $-D . dc/dx$. If the diffusion velocity is u_D, the amount in gram ions transferred per second is also $u_D c$, where c is the concentration in gram ions per cc.

Hence,

$$u_D . c = - D \frac{dc}{dx}, \qquad (12)$$

and therefore

$$u_D = - \frac{D}{c} \frac{dc}{dx} . \qquad (13)$$

This value for the diffusion velocity can then be substituted in the equation for the viscous resistance offered to the passage of the ions and this is given by Stokes' Law as

$$6\pi r \eta u_D = - 6\pi r \eta \frac{D}{c} \frac{dc}{dx} . \qquad (14)$$

The driving force in diffusion was shown by Einstein on quite other grounds to

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[1] Fick's Law should be concerned, strictly, with activity gradients. The relevant activities are, however, usually small, and are assumed here to be identical with the values of the concentration.

be also given by

$$-\frac{kT}{c}\frac{dc}{dx}.\tag{15}$$

In the steady state it therefore follows that:

$$-\frac{kT}{c}\cdot\frac{dc}{dx}=-6\pi\,r\,\eta\,\frac{D}{c}\frac{dc}{dx}.\tag{16}$$

Or,

$$\frac{kT}{D}=6\pi\,r\,\eta\,.\tag{17}$$

Considering, now, the *electrolytic* migration of the ions at infinite dilution, where the interionic forces can be neglected, the equation governing motion in a steady state is

$$X\,z_i\,e=6\pi\,r\,\eta\,v\,,\tag{18}$$

where X is the applied electric field, z_i the valency of the ion, and v the ionic velocity. Hence,

$$\frac{z_i\,e}{u_i}=6\pi\,r\,\eta\tag{19}$$

where u_i is the ionic mobility.

Equations (17) and (19) both refer to the transport of the ions in one and the same solution and hence are comparable, so that

$$D=\left(\frac{kT}{z_i\,e}\right)u_i\,.\tag{20}$$

But

$$\lambda_i=z_i\,F\,u_i\,,\tag{21}$$

where λ_i is the limiting equivalent conductance of the ith ionic species. Hence,

$$D=\frac{kT}{z_i^2\,e_0}\frac{\lambda_i}{F}=\frac{RT}{z_i^2\,F^2}\,\lambda_i\,.\tag{22}$$

Thus, substituting the value for D into (11) and extracting δ, one obtains

$$\delta=\left(\frac{R}{z_i F}\right)\frac{\lambda_i\,T\,c}{i_L}\,,\tag{23}$$

so that the thickness of the diffusion layer can be obtained essentially from an experimental determination of the limiting current, the other terms generally being known. The numerical evaluation of equation (23) with R in joules, *i.e.* 8·313, and F in coulombs, *i.e.* 96,500, gives the thickness of the diffusion layer in cms. according to the equation

$$\delta=8\cdot62\,.\,10^{-5}\frac{\lambda_i\,T}{z_i\,i_L}\,c\text{ cm.},\tag{24}$$

with the concentration in g.ions per cc. of solution.

For various types of electrode processes (*e.g.* redox processes, deposition of metals, discharge of anions, etc.) the value of δ, obtained by the application of equation (24), is 0·05 cm., in *unstirred* aqueous solution. Mechanical agitation of the solution and increase of its temperature reduce the value of δ which, for vigorous agitation, may reach a limiting value of about 0·001 cm. The effect of temperature is relatively small. Reference to equation (9) shows that decrease in δ results in increase of i_L, *i.e.* the limiting current density for the deposition of a given species can be raised considerably whilst still maintaining 100% current efficiency. Efficient agitation of

the solution is therefore always maintained in, for example, metal deposition processes.

Knowledge of the value of δ enables an approximate numerical equation to be evaluated for i_L in terms of the activity and the valency of the given ion. Thus, in equation (24), λ_i is about 50 ohms^{-1}cm.^{2} for many electrolytes in solutions of medium concentrations and the mean value of the diffusion coefficient for a number of substances is $1 \cdot 3 \cdot 10^{-5}$ cm.^{2}sec.$^{-1}$, so that taking δ as about 0·05 cm. at 20° it follows by rearrangement from (24) that the limiting current is given approximately for these substances by

$$i_L = 0 \cdot 025 \, z \, c \quad \text{amps per sq.cm.} \tag{25}$$

The concentration in the above approximate equation is expressed in gram ions or moles *per litre*. This equation enables i_L to be calculated roughly for a given deposition process and this process then occurs with 100% efficiency until the limiting current is exceeded, when the current efficiency of the process falls off, and another process begins to take place.

(iii) *The Diffusion Controlled Current at a Moving Surface*

The most well known and practically important case of a diffusion controlled current at a non-stationary surface is that of the dropping mercury electrode (see p. 408). Two principal modifications have to be made to the equations deduced for a stationary surface. Firstly, the area of the drop is changing continuously. The expression for the current strength, I, at such an electrode can be calculated from equations (7) and (11) if a term is inserted for the area A_t of the drop at a given instant, t.

Hence,

$$I = \frac{z \, F \, D \, A_t}{\delta n} (a - a_s). \tag{26}$$

A_t can be expressed in terms of the drop rate of the mercury. Let this be v ml. per second. Then, it is clear that t sec. after the beginning of the formation of a drop, assuming this to be spherical and of radius r_t,

$$\tfrac{4}{3} \pi r_t^3 = v \, t. \tag{27}$$

$$\therefore \quad A_t = 4 \pi r_t^2 = 4 \pi \left(\frac{v \, t}{\tfrac{4}{3}\pi} \right)^{2/3}. \tag{28}$$

Secondly, the value of δ changes with time. It can be shown from Fick's second Law of diffusion that if the area of the drop is maintained constant, δ depends upon time according to the equation $\delta = \sqrt{\pi D t}$. Taking into account the rate of growth of the drop shows that δ becomes

$$\delta = \sqrt{\tfrac{3}{7} \pi D t},\qquad (29)$$

the factor $\sqrt{\tfrac{3}{7}}$ being independent of the drop rate. It follows, therefore, from (26) that the current strength at a time t is given by

$$I_t = \frac{z\,F\,D\,4\,\pi}{t\,(\tfrac{3}{7}\,\pi\,D\,t)^{1/2}} \left(\frac{v\,t}{\tfrac{4}{3}\,\pi}\right)^{2/3} (a - a_s) \qquad (30)$$

$$= 4 \cdot 168 \, z\,F\,D^{1/2}\,v^{2/3}\,t^{1/6}\,(a - a_s). \qquad (31)$$

The dependence of the current upon time during the growth of a drop has been confirmed by experiments carried out with a short period torsion galvanometer. With a long period galvanometer, the mean current $\bar{I}$ during the drop time τ is registered and is given by the equation

$$\frac{1}{\tau}\int_0^\tau I_t\, d\tau = 3 \cdot 572\, z\,F\,D^{1/2}\,v^{2/3}\,\tau^{1/6}\,(a - a_s), \qquad (32)$$

i.e. $\bar{I}$ is independent of time at a given drop rate, v.

Equation (32) is similar to that first deduced in a different manner by ILKOVIC [1] and is an essential part of the theory of the current-voltage relation at a dropping mercury electrode, thus forming part of the theoretical basis of polarography (see 408)[2].

(iv) *Concentration Overpotential at a Stationary Surface*

If the rate of the electrode reaction is governed by the diffusion of ions to the electrode surface and all other electrode processes at the given electrode are rapid, then, the cathode potential at a current density, i, will be almost identical with the reversible value of the electrode potential with an ionic activity of a_s, the value *at* the electrode surface. Hence,

$$e_i = e_0 + \frac{RT}{zF}\ln a_s. \qquad (33)$$

To obtain the concentration overpotential, η_c, it is necessary to subtract from e_i the reversible electrode potential, *i.e.* the value

[1] D. ILKOVIC, *Coll. Czech. Chem. Comm.*, 1934, **6**, 498.

[2] A comprehensive discussion of diffusion controlled currents at various types of surfaces is given by B. LEVICH, *Faraday Soc. Discussion*, 1947, No. 1, 37.

with the ionic activity, a, in the bulk of the solution. Hence,

$$e_r = e_0 + \frac{RT}{zF} \ln a. \tag{84}$$

Thus,

$$\eta_c = e_i - e_r = \frac{RT}{zF} \ln \frac{a_s}{a}. \tag{85}$$

From equations (7 and 10), it follows that:

$$\frac{a_s}{a} = \frac{k\,a - i}{k\,a}, \tag{86}$$

where $k = \dfrac{D\,z\,F}{\delta\,t}$, so that

$$\eta_c = \frac{RT}{zF} \ln \frac{k\,a - i}{k\,a}. \tag{88}$$

Also from (10), $i_L = k\,a$. Hence,

$$\eta_c = \frac{RT}{zF} \ln \frac{i_L - i}{i_L}. \tag{89}$$

From equation (39) it can be seen that at a given value of i, the value of η_c decreases with increase of the concentration. Increase of k also causes a reduction in η_c and this can be achieved either by a reduction in δ or by an increase in D. As noted above, the diffusion layer thickness is considerably reduced by stirring of the electrolyte. D can be increased for a given ionic species by increase in temperature.

If k and a, and hence i_L, are maintained constant, it can be shown by expansion of the logarithmic term in (89) that η_c is linear with i for small values of i. As i increases, it must approach i_L and when $i =$ it follows from (89)
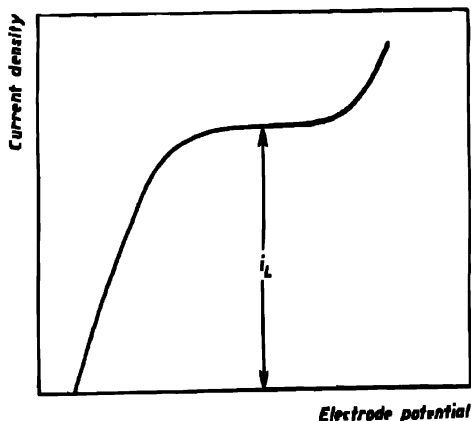
Fig. 65. Current density-potential relation for an electrode exhibiting concentration overpotential

that the concentration overpotential theoretically becomes equal to —∞, corresponding to the condition at which a_s for the ion undergoing deposition becomes equal to zero.

In practice, an abrupt change in the potential of the cathode takes place to a more negative value at which some other ion (*e.g.* the hydrogen ion if the solutions contain only one metal ion) begins to deposit. The current density again increases with increase of potential, as shown in Fig. 65). Thus the limiting current density, i_L, signifies the maximum rate at which a given ion can be discharged under the given experimental conditions.

(v) *Polarography*

The current-voltage curve arising at an electrode exhibiting concentration overpotential can be used as a means of quantitative and qualitative analysis of substances capable of undergoing cathodic reduction or anodic oxidation. For this purpose, a dropping mercury electrode is used in preference to a stationary electrode and the apparatus in which such current-potential curves are measured is called a polarograph.

Use of a dropping electrode has two advantages: (a) the constant renewal of the surface eliminates passivity or poisoning effects; and (b) the high overpotential of hydrogen on mercury renders possible the deposition upon the dropping mercury electrode of substances as difficult to reduce as, for example, the alkali ions. The dropping mercury electrode is effective over the potential range +0·4 to —1·8 volts, referred to the normal hydrogen scale. Above about 0·4 volts [1], mercury dissolves and at potentials more negative than —1·8, visible hydrogen evolution occurs.

The cathodic and anodic processes in a cell involving a dropping mercury electrode are conveniently separated by making one of the electrodes very large compared with the other. This means that the c.d. across it is very low compared with that at the smaller electrode, which is more readily polarisable and is hence the determining electrode in the current-potential relation. The potential of the anode can thus be regarded as constant and if

[1] J. REVENDA, *Coll. Czech. Chem. Comm.*, 1934, **6**, 453; I. M. KOLTHOFF and C. S. MILLER, *J. Am. Chem. Soc.*, 1941, **63**, 1405.

this is measured by comparison with a standard electrode the potential of the cathode can be determined from the total potential difference across the poles of the cell. This latter potential difference includes an ohmic potential drop, but since the current is generally small (*i.e.* of the order of 10^{-5} amp.) it can usually be neglected. A large calomel electrode is sometimes used as a separate anode as the calomel electrode is less likely to become polarised than the ordinary mercury anode. Knowing the constant potential of the calomel electrode, that of the cathode is evaluated from the total potential difference across the polarographic cell. In polarography the potential of the normal calomel electrode is usually taken as the arbitrary zero of potential. When the anode is a normal calomel electrode it follows that the applied potential difference is always equal and opposite to the cathode potential on the normal calomel scale.

The schematic arrangement of a polarograph is shown in Fig. 66, where the anode is a layer of mercury at the bottom of the beaker and the cathode is mercury dropping from the capillary. The potentiometer BC enables a variable potential difference to be applied and the current strength is measured by the galvanometer, which is generally connected in parallel with a shunt, to permit the sensitivity to be altered at will. In the automatically recording polarograph, which is nearly always used in the analytical applications of polarography, the potentiometer wire is mounted on a drum and the movement of the contact E is coupled with the rotation of

Fig. 66.
Schematic diagram of arrangement for polarographic analysis

another drum, which photographically records the current by means of light reflected from the galvanometer mirror (see p. 584).

The current-voltage curves for the dropping mercury electrode

in a pure normal solution of potassium chloride and in a normal solution of potassium chloride containing small amounts of Pb¨, Cd¨ and Zn¨ ions are shown in Fig. 67. After reaching the deposition potential for each type of ion on mercury, the current strength increases rapidly until it is once again practically constant (*i.e.* has reached the limiting current) with further increase of potential. The polarogram thus shows a series of steps or waves, each indicating the presence of a reducible ionic species. The sections of the curve parallel to the abscissa comprise pure diffusion currents, as the presence of an indifferent electrolyte in excess reduces the number of ions brought up to the electrode by electrolytic transport almost to zero (see p. 402). Consequently, every solution to be analysed has electrolyte added (usually KCl) in about one hundred times excess, thus ensuring that the reducible ions arrive at the electrode virtually only by diffusion, *i.e.* independently of their charge or transport numbers.

Fig. 67. Current-potential curves for (lower curve) a 1*N* KCl solution; and (upper curve) a 1*N* KCl solution containing heavy metal ions

The order of the deposition potentials of the various ions (*e.g.* from solutions of unit activity) is not the same as the electrochemical series, because some metals deposited at the cathode become amalgamated and the activity of the metal in the mercury affects the deposition potential. It is, however, possible to deposit practically all cations (including the alkali metal ions) on the dropping mercury electrode, and thus to enable them to be identified and estimated.

The quantitative analysis of a given species follows from the determination of the limiting current for the deposition of that species, which can be obtained from the polarogram (the current-potential relation in a polarographic cell). Thus, in (32) the

factors on the right hand side excepting the activity term can be maintained approximately constant during change of the latter, particular care being taken with regard to temperature control, owing to the strongly temperature dependent nature of the diffusion coefficient. It is not customary to evaluate "a" numerically from (82) but rather to determine the constant in front of "a" empirically from a determination of i_L in the presence of a known amount of a given ionic species. This avoids errors in the calculation of the theoretical constant due to adsorption of ions on the mercury and neglect of interionic forces in the double layer [1]. Quantitative estimation of various species in solution can be made for concentrations of a given species as low as 10^{-6} gram ions per litre, and as the currents involved are small the change in concentration of a species in the bulk of the solution during the execution of one polarogram is negligible, so that several analyses can be made of the same solution.

The identification of the species present in solution depends upon a knowledge of a quantity characteristic of that species and termed its *half-wave potential*. An approximate explanation of the significance of the half-wave potential can be given as follows. At the bottom of the current-potential wave (see Fig. 65), the solution at the electrode surface can be regarded as containing the "oxidised form" (*e.g.*, quinone, or Na$^{\cdot}$) whereas at the top of the curve this has been converted entirely into a "reduced" form (*e.g.*, hydroquinone, or sodium amalgam). Then, the potential of the mercury electrode can be written (VII, 76), as

$$e = e_0 + RT \ln \frac{a_{Ox.}}{a_{Red.}},$$

where $a_{Ox.}$ and $a_{Red.}$ are the activities of the oxidised and reduced forms of the entity undergoing reduction at the dropping mercury electrode. It follows, therefore, that considering the position when a given wave is *half* completed, $a_{Ox.} = a_{Red.}$, and $e = e_0$, the half wave potential (sometimes written as $e_{1/2}$). The latter potential is,

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[1] In the "constant" term in equations (31 and 82), v and t vary to some extent because of the changes in surface tension corresponding to changes in cathode potential. For the small change in potential corresponding to the deposition of one ionic species, however, they can be taken as constant.

therefore, experimentally determined by finding the potential which corresponds to the middle point of the current-potential relation during reduction of an entity. As, at the half-wave potential, the term containing activities is always zero, it is immaterial what the concentrations are, *i.e.* the half-wave potential is independant of concentration and is only characteristic of the reaction occurring. Knowledge of the half-wave potential, therefore, gives a characteristic quantity by which the substance can be identified. It is in this way that polarography can be used in qualitative analysis.

The half-wave potential associated with the deposition of a metal ion which forms an amalgam with mercury is the oxidation-reduction potential of the reaction $M^{z+} + z\,e \rightleftarrows M$. If, therefore, the deposited metal atoms formed an ideal solution in mercury, it would also be the standard electrode potential e_0 of the metal. Accordingly, $e_{1/2}$ is not identical with the standard potential of the pure metal, but deviates therefrom by an amount depending on the affinity of the metal for mercury. As a result, the alkali and alkaline earth metals, for example, have half-wave potentials considerably more positive than their standard potentials. In table 35 the normal potentials of table 22 (recalculated with the normal calomel electrode as reference zero) are compared with the corresponding half-wave potentials at the dropping mercury electrode.

TABLE 35

HALF-WAVE AND NORMAL POTENTIALS FOR VARIOUS CATIONS WITH REFERENCE TO THE NORMAL CALOMEL ELECTRODE

Ion	Li'	Cs'	K'	Rb'	Ca''	Na'	Mg''	Zn''	Fe''
e_0	—3·29	—3·20	—3·19	—3·19	—3·03	—2·98	—2·62	—1·03	—0·71
$e_{1/2}$	—2·31	—2·09	—2·17	—2·07	—2·23	—2·15	— 1·9	—1·00	—1·33
$e_{1/2} - e_0$	0·98	1·11	1·02	1·12	0·80	0·83	0·72	—0·03	—0·62

Ion	Cd''	Tl'	Co''	Ni''	Sn''	Pb''	H₃O'	Cu''
e_0	—0·67	—0·61	—0·55	—0·51	—0·41	—0·40	—0·27	+0·08
$e_{1/2}$	—0·63	—0·50	—1·23	—1·09	—0·47	—0·46	—1·60	—0·03
$e_{1/2} - e_0$	0·04	0·11	—0·68	—0·58	—0·06	—0·06	—1·33	—0·11

The difference $e_{1/2} - e_0$ corresponds to the standard potential of a cell,

Metal | Metallic salt solution | Metal-amalgam

and is a measure of the free energy of amalgam formation from metal and mercury under standard conditions. From the relation $\Delta G = -n_s E F$, it follows that amalgam formation occurs spontaneously with the alkali and alkaline earth metals and that the affinity of these metals for mercury is large. Conversely, the free energies of amalgam formation of the iron group are positive which is connected with the fact that here, as in the case of hydrogen evolution at a mercury cathode, deposition is associated with a marked irreversible polarisation (*i.e.* a large overpotential). The half-wave and standard potentials are thus not comparable in these cases.

Dissolved oxygen also gives a polarographic half-wave potential which may be used for the quantitative determination of dissolved oxygen in a solution down to concentrations of 10^{-6} gram mols per litre. In the analysis of other substances it is necessary to remove most of the oxygen from the solution to be analysed by passage of oxygen-free hydrogen or nitrogen gas, and thus avoid interference from the polarographic half-wave of oxygen.

Not only inorganic ions but also organic substances with reducible groups can be estimated; and this may be carried out in a mixed solution containing both ions and the organic substance. The method has been used in the quantitative estimation of aldehydes, ketones, nitro compounds, sugars, *etc.* In recent years the detection of certain diseases giving rise to tissue destruction has been accomplished polarographically. Thus, blood serum gives a specific polarographic half-wave potential in the presence of cobaltic ions, ammonia and ammonium chloride, due to the presence in a protein of a cystein group which forms a complex with the cobaltammines present. The wave is present in all blood serums but increases characteristically in the presence of cancer and some other diseases[1].

The range of applicability of the polarograph has become increasingly wide in recent years. In pure research it has been used

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[1] R. BRDICKA, *Research*, 1047—8, 1, 25.

in the examination of the kinetics of reactions in solution, for the determination of the solubility of sparingly soluble substances, in the examination of tautomeric and complex equilibria, *etc.* It has also become the instrument for the rapid analysis of solutions containing several ionic species. In this capacity its accuracy is less than that of classical chemical analysis but often sufficient, particularly for routine laboratory tests or in industrial practice.

(vi) *Depolarisation of Hydrogen Deposition by Oxygen*

From equation (25), the limiting current density for the diffusion of a depolariser to an electrode in an unstirred solution at 17 °C can be shown to be given approximately by the equation $i_L = 0{\cdot}020 \, z \, c$ amp./sq.cm., where c is the concentration of the depolariser in gram ions (or mols)/litre and z is the number of electrons transferred in the reduction at the cathode. At 17 °C,, the absorption coefficient of oxygen in water has the approximate value of $0{\cdot}038$, whence $c = 38/22{,}400$ for an aqueous solution in equilibrium with oxygen, and $z = 4$. Hence the value of i_L for the diffusion of oxygen to the cathode in such a solution is $0{\cdot}020 \, . \, 4 \, . \, 38/22{,}400 \simeq 10^{-4}$ amp./sq.cm. [1].

When the cathodic polarising current density has a value less than this, therefore, the hydrogen deposited at the cathode will be consumed immediately it is formed and the hydrogen overpotential will be considerably reduced. At a higher current density, *e.g.* 10^{-3} amp./sq.cm., the action of the depolariser accounts for only about 10% of the polarising current and thus reduces the effective c.d. for the deposition of hydrogen from 10^{-3} to $0{\cdot}9 \, . \, 10^{-3}$ amp./sq.cm. It will be shown below that the activation overpotential of hydrogen, upon which the rate of deposition of hydrogen depends, varies logarithmically with the current density and that for many cathodes a reduction of current density by a power of ten, decreases the overpotential by about $0{\cdot}1$ volt. The decrease in the effective polarising current density due to depolarisation by oxygen at 10^{-3} amp./sq.cm. would thus cause a diminution in the hydrogen overpotential of about $0{\cdot}005$ volt, which is less than

[1] A. HICKLING and F. W. SALT, *Trans. Faraday Soc.*, 1941, **37**, 319.

the experimental error (about ±10mv.) in the measurement of hydrogen overpotential. At current densities $> 10^{-3}$ amp./sq.cm., the diminution of overpotential caused by the presence of oxygen would be correspondingly less.

<center>(vii) <i>The Polarisation Capacity</i></center>

Knowledge of the diffusion equations applied to the problems of concentration overpotential in the present chapter enables some extension in the treatment of electrode capacities (p. 363) to be made. In Chapter X the capacity of the double layer was considered upon the assumption that it behaved as a condenser and that, consequently, during the charging process, a negligible number of ions crossed the electrode-solution interface. Some electrode systems do, in fact, function in this way (*e.g.* an Hg electrode in a solution of aqueous HCl) but in other systems there is little hindrance to passage of the ions from the solution to the electrode and in the reverse direction. This is the case, for example, when the ions in solution are those with which the electrode material can be in equilibrium, *e.g.* $Hg_2^{\cdot\cdot}$ ions for an Hg electrode. An electrode functioning under the limiting condition that *no* ions cross the double layer is termed a *completely polarisable* electrode and an electrode functioning under the limiting condition that the ions completely and freely pass across the double layer is termed a *non-polarisable electrode*. In fact, no electrode system is a perfect example of either limiting case. There is often some passage of ions across the double layer during charging so that the double layer behaves like a leaky condenser.

It is seen, therefore, that the current at the electrode has two functions. (i) The passage of ions to or from the electrode surface *across* the double layer; (ii) The charging up of the double layer. It will be shown below that the passage of ions to and/or from the electrode surface constitutes effectively a second capacitance (which is really a pseudo-capacitance as it does not involve the charging of a condenser) termed the electrolytic capacitance. The measured capacity of any acutal electrode system is thus the sum of the true double layer capacitance and the electrolytic (pseudo-)capacitance. By studying the dependence of the total capacitance on concentration and frequency in an A.C. field, a distinction can be made between these two capacitances and thus the double layer capacity can be determined even at an electrode-solution interface which is not completely polarisable [1].

Let the electrode be at a position $x = 0$ on the distance axis. Then the change in concentration per unit time at this point is given by

$$\frac{\partial c}{\partial t} = \frac{i}{F} + \frac{1}{F}\frac{\partial q}{\partial t} , \tag{40}$$

where i is the current density and q is the charge on the electrode at a time t.

[1] F. Krüger, Z. *Electrochem.*, 1010, **16**, 522; P. Dolin, B. Erschler and A. Frumkin, *Acta Physicochim. U.R.S.S.*, 1940, **13**, 793.

The second term on the right hand side of this equation represents the current necessary to charge up the double layer (condenser current) and the first term is the normal (faradaic) current.

If e represents the potential difference across the plates of the condenser, then

$$q = C e \quad \text{and} \quad e = \frac{RT}{F} \ln \frac{c}{c_0} . \tag{41}$$

If $Fe \ll RT$, *i.e.* for small values of e, the value of e can be written as

$$e = \frac{RT}{F} \left(\frac{c}{c_0} - 1 \right) . \tag{42}$$

Or,

$$\frac{\partial e}{\partial t} = \frac{RT}{c_0 F} \frac{\partial c}{\partial t} . \tag{43}$$

Hence,

$$\frac{\partial e}{\partial t} = \left(\frac{\partial e}{\partial c} \right)_{c = c_0} \frac{\partial c}{\partial t} = \frac{RT}{c_0 F} \frac{\partial c}{\partial t} . \tag{44}$$

Therefore,

$$\frac{\partial c}{\partial t} = \frac{i}{F} - \frac{1}{F} C \frac{RT}{c_0 F} \frac{\partial c}{\partial t} . \tag{45}$$

According to Fick's first law of diffusion, the rate of change of concentration with time is given by

$$- \frac{\partial c}{\partial t} = D \left(\frac{\partial c}{\partial x} \right)_{x = 0} . \tag{46}$$

Hence, in the stationary state, for which $dc/dt = -dc/dt$, it follows from (45) and (46) that

$$\frac{i}{F} = - D \left(\frac{\partial c}{\partial x} \right)_{x = 0} + \frac{C}{F} \frac{RT}{c_0} \frac{\partial c}{\partial t} . \tag{47}$$

The variation of the A.C. with time can be written as

$$i = i_0 \sin \omega t , \tag{48}$$

where $\omega = 2\pi\nu$ and ν is the frequency of the current. Further, according to Fick's second Law of diffusion,

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} . \tag{49}$$

From (47), (48) and (49), the limiting conditions for the solution of the diffusion equation are:

at $x = 0$,

$$\frac{i_0}{F} \sin \omega t = - D \left(\frac{\partial c}{\partial x} \right)_{x = 0} + \frac{C}{F} \frac{RT}{c_0} \frac{\partial c}{\partial t} ; \tag{50}$$

at $x = \infty$, $c = c_0$. The solution to (49) then becomes

$$c - c_0 = \frac{i_n}{\sqrt{D\omega/2}} \frac{i_n}{F} e^{\frac{x}{\sqrt{2D/\omega}}} \cos \left(\omega t - \frac{x}{\sqrt{2D/\omega}} + \theta \right) , \tag{51}$$

where

$$\tan \theta = \frac{1}{1 + \frac{C}{F} \frac{RT}{c_0} \sqrt{\frac{2\omega}{D}}} . \tag{52}$$

If c_0 is large,
$$\tan \theta = 1, \quad i.e. \quad \theta = 45°.$$

If c_0 is small,
$$\tan \theta = \frac{1}{\dfrac{C}{F} \dfrac{RT}{c_0} \sqrt{\dfrac{2\omega}{D}}}. \tag{53}$$

For small values of e and $x = 0$,
$$e = \frac{RT}{F} \left[\frac{c}{c_0} - 1 \right] = - \frac{i_0}{F} \frac{\sin \theta}{\sqrt{\dfrac{D\omega}{2}}} \frac{RT}{c_0} \sin \left[\omega t + \left(\frac{\pi}{2} - \theta \right) \right]. \tag{54}$$

The corresponding empirical result can be expressed in the form
$$e = \frac{i_0}{C'\omega} \sin \left[\omega t - \left(\frac{\pi}{2} - \theta \right) \right], \tag{55}$$

where $C' =$ double layer capacity plus electrolytic capacity.

Comparison of (54) and (55) shows that
$$C' = \frac{Fc_0}{RT} \sqrt{\frac{D}{2\omega}} \frac{1}{\sin \theta}. \tag{55}$$

Now for large concentrations ($\theta = 45°$), $\sin \theta = \dfrac{\sqrt{2}}{2}$, so that in this case
$$C' = \frac{F}{RT} c_0 \sqrt{\frac{D}{\omega}}, \tag{56}$$

which shows that the capacity is inversely proportional to the square root of the frequency. For small concentrations (c_0), $\sin \theta = \tan \theta$, which is given by (53) so that upon substitution one obtains
$$C' = C,$$

i.e. the total capacity becomes equal to the capacity of the double layer, and independent of frequency.

Experiments at a mercury electrode in aqueous solutions of mercurous nitrate in the presence of potassium nitrate confirm the theoretically indicated frequency variation at high concentration and show that at low concentrations of mercurous nitrate the capacity is in fact independent of frequency and has the same order as the double layer capacity.

B i b l i o g r a p h y : I. M. KOLTHOFF und J .J. LINGANE, *Polarography*, New York, 1941; M. J. ASTLE, *Polarography in Organic Chemistry, Trans. Electrochem. Soc.*, 1947, **92**, 523; J. HEYROVSKY, *Analyst*, 1947, **72**, 229; J. A. V. BUTLER *et al.*, *Electrical Properties of Interfaces in Physics, Chemistry and Biology*, Londen, 1951.

3. Activation Overpotential

(i) *Methods of Study of Reactions Involving an Activation Overpotential*

The earliest known cases of activation overpotential were those associated with the electrolytic evolution of hydrogen and oxygen. Although hydrogen and oxygen overpotentials are particularly large, appreciable activation overpotentials are associated with most electrode reactions, *e.g.* in metal deposition reactions or in the reactions of electrolytic reduction.

The phenomena of activation overpotential are difficult to measure accurately because they are easily affected by (I) the existence of minute traces of capillary active impurities and depolarisers; (II) the lack of reproducibility of metal surfaces, particularly in metal deposition processes, where the surface is continuously changing in area and properties during the deposition. Ordinary chemical methods are insufficient for the purification of solutions which must be carried out electrochemically by "pre-electrolysing" the solution with an auxiliary cathode so that impurities are deposited or adsorbed [1]. Relatively reproducible surfaces can be prepared by heating the electrode in a sealed glass bulb containing some appropriate gas (*e.g.* hydrogen) or a vacuum. The bulb can then be broken by a probe under the surface of the (already adequately purified) solution [2].

The following different methods give information upon the mechanism of reactions involving an activation overpotential.

(I) *Measurement of the dependence of the rate of the reaction* (i.e. *the current*) *upon potential*

In the use of this method the main conditions which can be varied are the temperature (heats of activation may be calculated from the temperature coefficient), the concentration of reacting species and the solvent.

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[1] A. M. AZZAM, J. O'M. BOCKRIS, B. E. CONWAY and H. ROSENBERG, *Trans. Faraday Soc.*, 1950, **46**, 918.

[2] J. O'M. BOCKRIS and B. E. CONWAY, *J. Sci. Instruments*, 1948, **25**, No. 8.

(II) *Measurement of the capacity of the electrode-solution interface at various frequencies*

By a comparing the variation of capacity and phase angle with frequency with certain theoretical expectations it is possible to gain information on the type of equivalent electrical circuit (*e.g.* condenser and resistence in parallel, *etc.*) to which the electrode-solution interface corresponds. It is also possible to measure in some cases the velocity of a single discharge process (*e.g.* $H^{\cdot} + e_0^- \rightarrow H$) as apart from that of the overall reaction rate (*e.g.* $2H^{\cdot} + 2e_0^- \rightarrow H_2$)[1].

(III) *Measurement of relation between quantity of electricity and potential during charging of the double layer*

The shape of the relation between potential and time of flow of current (which is proportional to the quantity of electricity passed during the charging up of the double layer at the electrode-solution interface) varies according to the rate controlling step in the evolution reaction. This method also gives results for the capacity of the metal-solution interface (see Chapter X, p. 860).

(IV) *Decay upon open Circuit*

In electrode processes involving gases, the type of relation between potential and time upon cessation of the current is characteristic of the amount of gas adsorbed on the metal.

(v) *Photochemical Methods*

Measurement of the dependence of the quantum efficiency of the photocurrent (*i.e.* the extra current caused to flow when light of suitable frequency strikes the electrode surface) upon frequency gives information as to whether or not electrode processes involve an electron transition as a rate determining process.[2] Results of such measurements made hitherto appear, however, to be somewhat difficult to interpret.

Application of these several methods shows that no one mechanism exists for the various types of activation overpotential and that the mechanism may even change for the same kind of overpotential (*e.g.*, hydrogen overpotential) when the metal is changed.

[1] B. Erschler, *Faraday Soc. Discussion*, 1047, No. 1, 269.

[2] P. J. Hilson and E. K. Rideal, *Proc. Roy. Soc.*, 1949, 199, 295.

In the following, the case of *hydrogen overpotential*, about which more material is available than for other examples of activation overpotential, will be discussed in detail.

(ii) *Experimental Results for Hydrogen Overpotential*

(I) *Dependence upon electrode material*

At a given current density, hydrogen overpotential on two or possibly three groups of metals decreases roughly in a parallel manner to the thermionic work function of the metal. (See Fig. 68). A corollary of this is that metals which adsorb hydrogen well (*e.g.* Pt) have a low overpotential for hydrogen evolution and the metals of lower adsorbing power have a higher hydrogen overpotential.
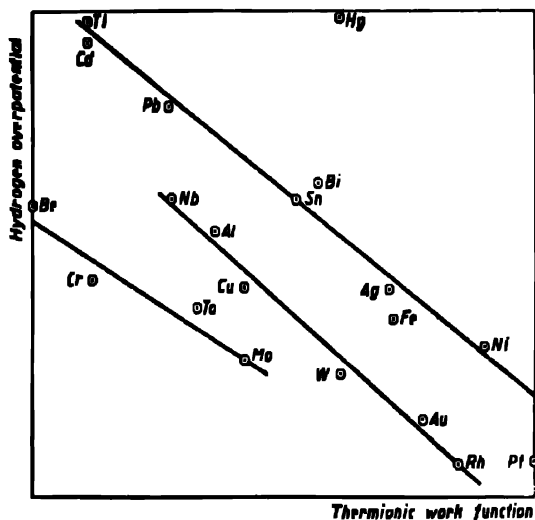
Fig. 68.
The relation between overpotential at 10^{-2} amp./ sq.cm. and the thermionic work function

(II) *Dependence upon current density*

The dependence of hydrogen overpotential upon current density is represented by an equation first empirically discovered by TAFEL, *i.e.*,

$$\eta = a - b \log i \,, \tag{57}$$

where a is a current density-independent term characteristic of the metal at a given temperature and varies from about -0.1 to -1.4 volts according to the metal. The constant b has a value of about $0.08 - 0.14$ depending upon the metal and most values of b are between the values $0.09 - 0.13$. [1] This constant is also

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[1] This refers to the values obtained in well purified solutions. In less pure solutions there is a greater spread of b values, which may rise to 0.3 or more.

written in terms of a corresponding constant a (for theoretical reasons, see p. 426) where $b = RT/aF$. Thus. a' varies approximately in pure solutions from about 2 to 0·4 for different metals; for many metals it has the value 0·5 approx. The TAFEL equation is valid over a large range of current densities, e.g. on mercury cathodes at least from 10^{-9} to 150 amp. per sq.cm. At low overpotentials the equation breaks down and the TAFEL line tends to become asymptotic to the current density axis (see p. 434).

(III) *Dependence upon temperature*

Hydrogen overpotential decreases with increase of temperature and the temperature coefficient is of the order of 10^{-3} volt per °C. There are two ways of expressing the variation of overpotential with temperature and these lead to slightly different values, U_I and U_{II}, of the heat of activation [1]. Thus, (1) the overpotential, η, at a temperature T is measured against a reversible hydrogen electrode under the same conditions, or (2) the cathode potential, e, is measured against a standard half cell at a fixed temperature T_0. As the current density is controlled by a rate process [see deduction of (70)], it follows that:

$$\left(\frac{\partial}{\partial T}\ln i\right)_\eta = \frac{U_I}{RT^2}; \quad \left(\frac{\partial}{\partial T}\ln i\right)_e = \frac{U_{II}}{RT^2}. \tag{58}$$

Now,

$$\frac{d}{dT}\ln i = \left(\frac{\partial}{\partial T}\ln i\right)_\eta + \left(\frac{\partial}{\partial \eta}\ln i\right)\frac{d\eta}{dT} \tag{59}$$

and hence

$$\left(\frac{\partial \eta}{\partial T}\right)_i = \frac{-U_1/RT^2}{\left(\dfrac{\partial}{\partial \eta}\ln i\right)_T}. \tag{60}$$

But from (57), and taking $b = RT/aF$,

$$\left(\frac{\partial}{\partial \eta}\ln i\right)_T = \frac{aF}{RT}, \tag{61}$$

[1] J. N. AGAR, *Faraday Soc. Discussion*, 1947, **1**, 81.

hence it is clear that

$$\left(\frac{\partial \eta}{\partial T}\right)_i = -\frac{U_I}{aFT};$$ (62)

and

$$\left(\frac{\partial e}{\partial T}\right)_i = -\frac{U_{II}}{aFT}.$$ (63)

Also, from (1),

$$\left(\frac{\partial \eta}{\partial T}\right)_i = \left(\frac{\partial e}{\partial T}\right)_i - \left(\frac{\partial e_r}{\partial T}\right)_i,$$ (64)

so that from (62), (63) and (64),

$$U_I - U_{II} = aFT\frac{\partial e_r}{\partial T}.$$ (65)

Thus, the difference between the two heats of activation is given in terms of the temperature coefficient of the reversible hydrogen electrode [1], which is not known, it being possible only to measure the net coefficient of the hydrogen electrode together with the thermojunction between the solution with which the working cathode is in contact and that with which the reference electrode is in contact. Hence, U_I, which is the fundamental heat of activation involved in overpotential, is accurately determinable only by measurement with method (1).

If a is constant with temperature, the heat of activation at the reversible potential is related to that at an overpotential of η by the equation

$$[\Delta H^*]_r^o = U_1 - a\eta F,$$ (66)

and from (62),

$$[\Delta H^*]_r^o = aF[T\left(\frac{\partial \eta}{\partial T}\right)_i - \eta].$$ (67)

In the following table, a number of typical results of measurements of $[\Delta H^*]_r^o$ are given for various metals.

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[1] P. T. GILBERT, *Faraday Soc. Discussion*, 1947, **1**, 320.

TABLE 86

HEAT OF ACTIVATION FOR THE ELECTROLYTIC EVOLUTION
REACTION $2H^. + 2e \rightarrow H_2$ AT VARIOUS CATHODES

Electrode material	Solution	a	$[\Delta H^*]_1^0$	Remarks
Hg	0·1N HCl	0·50	21·1	20°
	0·2N H$_2$SO$_4$	0·52	18·0	20°
	0·2N D$_2$SO$_4$	0·52	20·9	20°
	10N HCl	0·61	16·5	20°
	0·1N HCl in 100% methanol solution	0·56	19·7	20°
Ga	0·2N H$_2$SO$_4$	0·50	15·2	87° (liquid)
Woods alloy	0·2N H$_2$SO$_4$	0·40	16·4	87° (liquid)
Ni	0·1N HCl	0·49	5·0	20°
	NH$_4$Cl in liq. NH$_3$	0·49	7·0	—50°
Pt (bright)	0·2N H$_2$SO$_4$	0·75 - 0·3	9 - 12	20°; a decreases with time
Pt (bright)	0·2N NaOH	0·8 - 0·5	6 - 7	22°
Pd	0·2N H$_2$SO$_4$	0·5	0	Measurements very approximate
	0·2N NaOH	0·4 - 0·5	10	

(IV) *Dependence upon pH*

In dilute solutions, the hydrogen overpotential on metals of high overpotential (*e.g.* mercury, lead), is independent of pH up to solutions of acid strength about 0·1 N. At higher concentrations some decrease in overpotential occurs. For metals of lower overpotential, *e.g.*, nickel or platinum, the dependence on concentration begins at 0·001 N, overpotential decreasing with increase of concentration. Salts decrease the overpotential at a given current density and increase the dependence upon pH. Little work has been done on alkaline solutions. However, the limited information suggests that there is no essential difference in the overpotential behaviour compared with that in acid solutions.

(v) *Dependence upon solvent*

Hydrogen overpotential has been measured in methyl and ethyl alcohol, glycol, formic acid, acetic acid, ether and dioxan

and where possible mixtures of these substances with water. The effect of the solvent is a specific property of the electrode material. For metals of high overpotential there is a general tendency for the overpotential in the above mentioned non-aqueous solvents to be lower than that in water, particularly in the alcoholic systems. For metals of low overpotential, *e.g.* nickel, there is little difference between the overpotential in water and in the non-aqueous systems. For mixed solvents the *a* and *b* values of the appropriate TAFEL equations are considerably different from those in either pure compounds, particularly in the case of metals of high overpotential; thus for lead in methanolic solutions, the overpotential at a constant current density passes through a maximum at about 50% methanol.

(VI) *Dependence upon the initial quantity of electricity passed*

Measurements at mercury cathodes in oxygen-free solutions show a dependence of potential upon time which in the more positive region ($e_H > -0.3$) has a slope corresponding to a capacity of 50 μF/sq.cm. and in a more negative region corresponding to a capacity of about 18 μF/sq.cm., in agreement with the results of electrocapillary measurements upon the capacity of the double layer at the electrode-solution interface.

(VII) *Dependence upon "poisons"*

Certain substances, generally known as catalytic poisons, affect hydrogen overpotential when present in very small traces. The amounts of poison necessary to affect the overpotential at electrodes of low overpotential (*e.g.* nickel) are smaller than can be detected by chemical means and can only be removed by electrolytic deposition. The relation of overpotential to the amount of poison present is similar to that of an adsorption isotherm in gas catalysis.

(VIII) *Dependence upon diffusion of hydrogen through the electrode*

When the overpotential is measured upon the two sides of a foil electrode consisting of certain materials (*e.g.* iron or palladium), a "transfer" of overpotential takes place from the polarisation side of the foil (that upon which hydrogen is evolved) to the diffusion side. The slope of the TAFEL equation is lower (about 0.03 for iron)

upon the diffusion side of the foil than on the polarisation side (about 0·1 for iron)[1]. This result provides strong evidence that adsorbed hydrogen in large quantities (*i.e.* filling nearly the whole electrode surface) exists upon the polarisation side.

(iii) *The Theory of Hydrogen Overpotential*

(1) *The Tafel equation*

Suppose that the velocity of the cathodic reaction

$$2H^{\cdot} + 2e_0^- \rightarrow H_2$$

is $\overrightarrow{v}$. Then this reaction also occurs in the reverse direction at the cathode with a velocity of $\overleftarrow{v}$. When the electrode behaves reversibly, $\overrightarrow{v} = \overleftarrow{v}$. When it functions as a cathode, $\overrightarrow{v} > \overleftarrow{v}$, and when as an anode, $\overleftarrow{v} > \overrightarrow{v}$. In the electrolytic evolution of hydrogen, except at the lowest c.d.'s, the velocity of the reverse reaction, $H_2 \rightarrow 2H^{\cdot} + 2e_0^-$, can be neglected, *i.e.* $\overrightarrow{v} \gg \overleftarrow{v}$.

Without postulating any particular mechanism of hydrogen overpotential, *let it be assumed that the velocity of the rate determining reaction is controlled by particles having more than some minimum activation energy, U, and that the energy distribution is Maxwellian.* It is known from the fact that the rate of reaction (which is proportional to the current density) is increased when the cathode potential becomes more negative, that the energy of activation of the rate controlling reaction is affected by the electric field due to the cathode. If the cathode potential is e, then it is reasonable to suppose that the particles taking part in the rate controlling reaction are affected not by the whole cathode-solution potential difference, because this potential difference extends effectively over a distance of several Angström units from the cathode surface out into the solution and at the beginning of the rate controlling reaction the reacting particles may be inside this effective range of the cathode-solution potential difference. Let the part of the cathode-solution potential difference which affects the reaction be $(e - x)$. Then, the energy of activation becomes $U + (e - x) a F$, where a is a constant, namely the fraction

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[1] H. FISCHER and H. HEILING, *Z. Electrochem.*, 1950, **54**, 184.

of the potential $(e - x)$ which affects the rate of the reaction *towards* the cathode. U is the energy of activation at zero electrode solution potential difference.

The velocity of the evolution reaction must be proportional to the concentration of the reacting particles, c_A, c_B, ... which may be, for example, solvated protons or hydrogen atoms.

Hence,

$$\vec{v} = k(c_A, c_B \ldots) e^{-\dfrac{U + (e - x)aF}{RT}}, \qquad (68)$$

where k is a proportionality constant. As, except at very low current densities, $i = F\vec{v}$, then,

$$i = Fk(c_A, c_B \ldots) e^{\dfrac{U + (e - x)aF}{RT}}. \qquad (69)$$

Solution of this equation for e assuming U to be constant with change of current density, use of the defining equation for the overpotential [(1), p. 395], and the equation for the potential of the reversible hydrogen electrode in a solution of hydrogen ion activity a_H. gives

$$\eta = \frac{RT}{aF} \ln Fk + x - \frac{U}{aF} + \frac{RT}{aF} \ln (c_A, c_B \ldots) - \frac{RT}{F} \ln a_{H^+}$$
$$- \frac{RT}{aF} \ln i, \qquad (70)$$

which is of the same form as the TAFEL equation (57). It follows therefore that an equation of this form is a general consequence of the single assumption stated above. The various specific theories of the slow stage in the cathodic evolution reaction for hydrogen will now be considered.

(ii) *Specific theories of the slow stage*

Let the proton in solution be solvated by the base B (*e.g.* water) and the cathode material be represented by M. Then, the most important reactions to be considered are the following. The discharge reaction

$$BH^{\cdot} + e_0^- \overset{R_A}{\to} B + MH, \qquad (A)$$

in which the solvated proton, adsorbed on the cathode, is neutralised by an electron from the cathode at a rate R_A. This reaction

may be succeeded by two alternative methods of removing the atomic hydrogen from the surface of the electrode, namely the combination of adsorbed hydrogen atoms on the electrode

$$MH + MH \xrightarrow{R_B} 2M + H_2,\qquad\qquad\text{(B)}$$

or, alternatively, the removal of an adsorbed hydrogen atom by the arrival of a further solvated proton and its simultaneous neutralisation by means of an electron from the cathode, *i.e.*

$$BH^{\cdot} + MH + e_0^{-} \xrightarrow{R_C} B + M + H_2.\qquad\qquad\text{(C)}$$
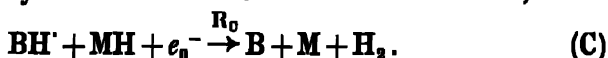
Thus, in the electrolytic evolution of hydrogen at various electrodes in acid solutions, reaction A always occurs initially. It may continue to occur, followed by B, or it may be followed by C, with which it then occurs simultaneously in order to maintain the concentration of adsorbed hydrogen atoms on the metal surface. If $R_A \ll R_B$ or R_C, then the reaction path will clearly consist of A followed by B, because C can only occur to an appreciable extent if $R_A > R_B$, whereupon the concentration of atomic hydrogen builds up upon the electrode surface. If $R_A > R_B$ or R_C then the reaction path consists of A followed by B or C according to whether $R_B > R_C$ or vice-versa.

The reactions A, B and C are called respectively the *discharge*, *catalytic* and *electrochemical reactions.*

(III) *The discharge reaction*

The reaction A can be considered upon the basis of the transition state theory of chemical reactions, according to which the specific rate of the transfer of a particle across an energy barrier is $\dfrac{kT}{h}\, e^{-\varDelta G^{*}/kT}$, where $\varDelta G^{*}$ is the standard free energy change in the creation of the activated complex $(\text{H}^{\cdot} \ldots e)$ from the initial state[1]. For the slow discharge reaction, the initial state can be considered to be the adsorbed, partly solvated protons in the HELMHOLTZ section of the electrical double layer, the final state being the hydrogen atoms adsorbed upon the electrode surface.

Hence, if the surface activity of the hydrogen ions adsorbed

[1] This assumes a value of unity for the transmission coefficient; *cf.* H. EYRING and W. F. K. WYNNE-JONES, *J. Chem. Phys.*, 1935, **3**, 492.

per sq.cm. of the double layer is a_+ the rate of the reaction is $a_+ \dfrac{kT}{h} e^{-\Delta G^*/kT}$, so that, as each ion carries one electronic charge, the number of charges passing to the cathode per second is $e_0 \, a_+ \dfrac{kT}{h} e^{-\Delta G^*/kT}$.

Hence,

$$i = e_0 \, a_+ \frac{kT}{h} e^{-\Delta G^*/kT} . \qquad (71)$$

The calculation of ΔG^* may now be considered, firstly in the special case in which there is no potential difference between the electrode and the bulk of the solution. It can be shown by means of thermodynamic cycles [1] that the heat content of the initial state is given by

$$H_I = I - \varphi - (L - L'), \qquad (72)$$

where I is the ionisation energy of the hydrogen atoms, φ is the work function of the metal electrode, L is the heat of hydration of the hydrogen ion and L' is a correcting term to this so that the change in heat content associated with the partial desolvation of the hydrogen ion as it approaches the electrode surface is taken into account. In a similar way it can be shown that the potential energy of the final state is given by

$$H_{II} = R - A, \qquad (73)$$

where R is the interaction energy between a hydrogen atom and a water molecule, and A that between an electrode and the adsorbed atomic hydrogen.

H_I and H_{II} are susceptible to numerical evaluation as a function of distance from the electrode and the kind of relation obtained is shown in Fig. 69 where A D represents the potential energy of the final state R — A and F G that of the initial state in the absence of an electrode-solution potential difference. Thus the equilibrium position in the initial state is the minimum of the curve F G and that of the final state the minimum of the curve A D. The hydrogen particle therefore has to pass over the energy col at X or some similar intersecting position (See below).

[1] R. PARSONS and J. O'M. BOCKRIS, *Trans. Faraday Soc.*, 1951.

In the application of the theory of absolute reaction rates, the rate determining quantities are

$$G^* - G_I = \Delta G^*, \text{ so that } \Delta G^* = H^* - H_I - T\Delta S^* ,$$

where $\Delta S^* = S^* - S_I$ and is equal to the difference in entropy between the activated and initial states, which can be approximately calculated by statistical mechanical means.

The effect of the existance of an electrode potential e at the cathode-solution interface may now be considered. This will have two main effects upon (71).

(i) It affects the surface activity of the adsorbed ions at the electrode-solution interface. If the thickness of the surface layer of ions is χ, then the surface activity in the absence of a double layer potential difference is given by $a_H \cdot \chi$, where $a_H \cdot$ is the activity of hydrogen ions in the bulk of the solution. However, if a potential difference exists at the interface, the ions adsorbed in the HELMHOLTZ section of the double layer will be at a potential ψ above that of the ions in the bulk of the solution (cf. STERN's theory of the electrical double layer, p. 368). Hence, according to the MAXWELL-BOLTZMANN law, the surface activity is not $a_H \cdot \chi$ but $a_H \cdot e^{-\psi F/RT} \chi$; equation (71) can now be rewritten as

$$i = e_0 \, a_H \cdot e^{-\psi F/RT} \, \chi \, \frac{kT}{h} \, e^{-\Delta G^*/kT} . \tag{74}$$

Fig. 69.
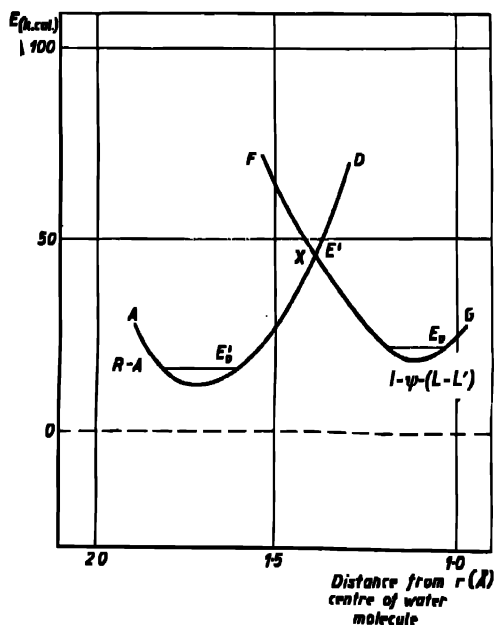
The variations of certain potential energy functions with distance for the discharge of hydrogen ions onto a metal electrode

(II) It affects the energy of the initial state of the reaction. Thus, the energy of the ions is increased by the quantity $(e - \psi) F$. The free energy-distance relation for the initial state is shown in Fig. (69) by the curve FG. The vertical distance moved by the point of intersection of the curves of the initial and final state can be shown geometrically to be $(1 - a) (e - \psi) F$, where a is the quantity

$$\frac{g_{\text{initial}}}{g_{\text{initial}} - g_{\text{final}}} = a , \tag{75}$$

g being the gradient of the relation to distance of the energy of the indicated state. It follows that the change in free energy in the formation of the activated state (represented by the point X) is altered by an amount

$$(1 - a) (e - \psi) F - (e - \psi) F, = -a (e - \psi) F,$$

when a potential difference e exists at the metal-solution interface. Equation (74) may now be written in the form

$$i = e_0 \, a_{\text{H}^\cdot} e^{-\psi F/RT} \chi \frac{kT}{h} e^{-\{\Delta G^* + a(e - \psi)F\}/kT} . \tag{76}$$

$$\therefore \; \ln i = \ln e_0 \chi \frac{kT}{h} e^{-\frac{\Delta G^*}{RT}} + \ln a_{\text{H}^\cdot} - \frac{\psi F}{RT} - a (e - \psi) \frac{F}{RT} . \tag{77}$$

$$\therefore \; e = \frac{RT}{aF} \ln e_0 \chi \frac{kT}{h} e^{-\frac{\Delta G^*}{RT}} + \frac{RT}{aF} \ln a_{\text{H}^\cdot} + \left(1 - \frac{1}{a}\right) \psi . \tag{78}$$

Using (1) and (VII, 49), it follows that:

$$\eta = \frac{RT}{aF} \ln e_0 \chi \frac{kT}{h} e^{-\frac{\Delta G^*}{RT}} + \left(\frac{1}{a} - 1\right) \frac{RT}{F} \ln a_{\text{H}^\cdot} +$$
$$+ \left(1 - \frac{1}{a}\right) \psi - \frac{RT}{aF} \ln i , \tag{79}$$

Also, using the relation between ψ and $a_{\text{H}^\cdot}$ (p. 368), the over-potential in dilute solutions becomes

$$\eta = \frac{RT}{aF} \ln e_0 \chi \frac{kT}{h} e^{-\frac{\Delta G^*}{RT}} + \left(1 - \frac{1}{a}\right) \psi_0 - \frac{RT}{aF} \ln i . \tag{80}$$

Numerical substitution in this equation gives results in agreement with experiment for mercury electrodes within the limits of un-

certainty of the theoretical values brought about by difficulty in obtaining exact values of R and A.

When the rate of the overall hydrogen evolution reaction is controlled by the slow discharge of protons, then the following characteristics would be expected. The dependence of overpotential at a given current density upon the electrode material should vary in a way parallel to the heat of adsorption of hydrogen upon the metal. The overpotential would thus tend to be high for metals having a low heat of adsorption of hydrogen and low for metals on which hydrogen is strongly adsorbed. No limiting current would be expected and the overpotential should be independent of pH, as shown in (80), so long as the STERN equation is still applicable, *i.e.* up to medium concentrations of about $1N$. The solvent effect depends upon relative degrees of adsorption of solvent molecules on cathode and reference electrode and it can be shown[1] that a change from aqueous to alcoholic solution would bring about a lowering of overpotential, in accordance with the facts. The linearity of the relation between potential and time in the charging curve is clearly in accord with the theory, according to which the ions would build up until a certain potential difference existed across the double layer before discharging to an appreciable extent. The effect of traces of poisons would be less marked for a metal at which reaction A was the effective rate controlling step than one for which B is the rate controlling reaction because of the absence of important active centres open to specific poisoning in the first case. Lastly, it is obvious that no "transfer" of overpotential through an electrode can take place if A is the effective mechanism because if B or C are faster than A, a large concentration of adsorbed hydrogen atoms does not build up on the polarisation side of the electrode surface.

(IV) *The catalytic reaction*

The expression for the rate of the combination reaction between two hydrogen atoms on the metal surface can be written in the form

$$v_B = a_H{}^2 \frac{kT}{h} e^{-\Delta G^*/kT}, \qquad (81)$$

where ΔG^* is the free energy of the formation of the activated complex in the combination reaction between the two hydrogen atoms, and a_H is the activity of the hydrogen atoms per sq.cm. In this case, $i = 2e_0 v_B$, so that

$$i = 2e_0 a_H{}^2 \frac{kT}{h} e^{-\Delta G^*/kT}. \qquad (82)$$

In this equation, ΔG^* can be written as $\Delta G_0{}^* + a_2 eF$, where a_2 is a complex factor depending mainly upon the repulsion energy

[1] J. O'M. BOCKRIS and R. PARSONS, *Trans. Faraday Soc.*, 1948, **44**, 860; 1949, **45**, 916.

between two hydrogen atoms adsorbed on the metal surface. It can be shown from a statistical mechanical examination of the surface reaction that at low concentrations of hydrogen a_a has the value 2 but when the surface approaches saturation a_a decreases rapidly towards zero [1]. Thus, except at very high current densities,

$$i = 2e_0 a_H^2 \frac{kT}{h} e^{-(\Delta G^* + 2eF)/RT} . \tag{83}$$

Use of equations (1) and (VII, 49) leads to the evaluation of η from the above equation as

$$\eta = \frac{RT}{2F} \left[\ln 2e_s \frac{kT}{h} - \frac{\Delta G^*}{RT} \right] + \frac{RT}{F} \ln \frac{a_H}{a_{H^.}} - \frac{RT}{2F} \ln i . \tag{84}$$

The variation of overpotential with the cathode material can easily be understood upon the catalytic theory, for there is a general tendency for the overpotential at a given current density to decrease with increase of catalytic power of the metal. This follows because a metal of high catalytic power would bring about a rapid combination of hydrogen atoms on the electrode surface so that a comparatively large current can pass at a small overpotential.

The slope of the TAFEL equation can be seen from equation (84) to be $\frac{RT}{2F} . 2 \cdot 303 = 0 \cdot 029$ at 25°C., except at very high current densities when the value of a of equation (84) tends towards zero. The effect of pH is indefinite upon this mechanism owing to concomitant changes which may take place in c_H and ΔG_s^* with pH and overcome the apparent increase of overpotential by $0 \cdot 058$ volts with every decrease of one unit of pH which the above equations would otherwise indicate. The relation between the quantity of electricity passed and electrode potential would be non-linear if the reaction B is rate determining. In addition, owing to the existence of active centres upon the electrode, a marked sensitivity to very minute traces of poisons would be expected, owing to the importance of active centres in determining the rate of the reaction. Transfer of overpotential through an electrode would be possible if this mechanism is applicable but need not be necessarily observable as the diffusion velocity may be very slow.

(v) *The electrochemical reaction*

The kinetics of the electrochemical desorption mechanism are more complex than those of the other two reactions at a working hydrogen electrode owing to the fact that two discharge processes

[1] J. HORIUTI, G. OKOMOTO and K. HIROTA, *Sci. Papers Inst. Phys. Chem. Res.* (Tokyo), 1936, **29**, 223; an alternative theory is given by A. HICKLING and F. W. SALT, *Trans. Faraday Soc.*, 1942, **38**, 474.

occur simultaneously to maintain the concentration of hydrogen adsorbed upon the electrode surface.

The equation for the velocity of the discharge of solvated protons onto a metal surface containing n adsorption centres takes place according to the reaction

$$BH^{\cdot} + e_0^- \rightarrow MH,$$
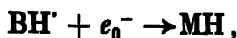
and can be written in the form

$$R_A = k_1 \left(1 - \frac{a_H}{n}\right) a_{H^{\cdot}} \cdot e^{-\psi F/RT} \, e^{-a(e-\psi)F/RT} , \qquad (85)$$

where a_H is the concentration of the atomic hydrogen upon the electrode surface, $a_{H^{\cdot}}$ is the hydrogen ion concentration in the bulk of the solution, k_1 is a velocity constant and a has an analogous meaning to that given by (75).

The rate of the reverse ionisation reaction

$$MH \rightarrow BH^{\cdot} + e_0^{\cdot\cdot}$$

is given by

$$R_D = k_2 \frac{a_H}{n} e^{-a(e-\psi)F/RT} \qquad (86)$$

and that of the electrochemical desorption process

$$BH^{\cdot} + MH + e_0^- \xrightarrow{R_C} B + M + H_2$$
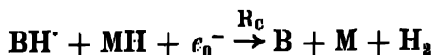
by

$$R_C = k_3 \frac{a_H}{n} a_{H^{\cdot}} \cdot e^{-\psi F/RT} \, e^{-a(e-\psi)F/RT} . \qquad (87)$$

In the stationary state

$$R_1 - R_2 - R_3 = 0 ,$$

from which it follows that:

$$\frac{a_H}{n} = \frac{k_1 a_{H^{\cdot}} \cdot e^{-\psi F/RT}}{k_1 a_{H^{\cdot}} \cdot e^{-\psi F/RT} + k_2 e^{(e-\psi)F/RT} + k_3 a_{H^{\cdot}} \cdot e^{-\psi F/RT}} . \qquad (88)$$

The current due to the electrochemical mechanism is given by

$$i = 2F k_3 \frac{a_H}{n} a_{H^{\cdot}} \cdot e^{-\psi F/RT} \, e^{-a(e-\psi)F/RT} . \qquad (89)$$

Substituting for a_H/n and assuming that the cathode potential is not near to the reversible potential one obtains

$$i = 2F \frac{k_1 k_3}{k_1 + k_3} a_{H^\cdot} e^{-\psi F/RT} e^{-a_1(e-\psi)F/RT} \ . \qquad (89)$$

The overpotential, η, can then be evaluated from this equation by use of (VII, 49) and the STERN relation between ψ and $a_{H^\cdot}$. It follows that:

$$\eta = \frac{RT}{aF} \ln \frac{2F k_1 k_3}{k_1 + k_3} - \frac{RT}{aF} \ln i \ . \qquad (90)$$

The value of a derived from this equation can be shown to be less than 1 although the numerical value for any given metal has not yet been accurately calculated.

The experimental behaviour indicated by the slow electrochemical mechanism is similar to that of the slow discharge mechanism with respect to limiting currents, initial quantity of electricity passed and effect of poisons. The overpotential should become pH-dependent at a lower hydrogen ion concentration than that for the discharge-controlled reactions, owing to the influence of the polar M–H bond. The electrochemical mechanism is to be distinguished from the discharge-controlled reaction principally by evidence indicating the covering of the surface with atomic hydrogen. This would be indicated, *inter alia*, by the variation of capacity with frequency and the transfer of overpotential through the electrode.

(VI) *Overpotential at low current densities*

In the theoretical derivations given above for mechanisms A, B and C it has been assumed that the cathode potential was not near to the reversible potential, *i.e.* that anodic currents such as $MH \rightarrow BH^\cdot + e_0^-$ in the slow discharge reaction can be completely neglected. When the potential is in the neighbourhood of the reversible potential this is no longer true. From (69), the cathodic current is given by

$$\overrightarrow{i} = K_1 e^{-(e-x) aF/RT} \ , \qquad (91)$$

where K_1 is a constant, if it is assumed that the energy of activation and the concentration of the entities taking part in the rate determining reaction are constant with change of current density.

The fraction of the potential difference $(e - x)$ which affects the anodic current will be that fraction which does not affect the cathodic current, *i.e.*, $(e - x)(1 - a)$.

Hence,

$$\overleftarrow{i} = K_2\, e^{(\epsilon - x)\,(1 - a)\, F/RT}, \tag{91a}$$

where K_2 is another constant.

The net (*i.e.* observed) current density, i, is given by

$$i = \overrightarrow{i} - \overleftarrow{i}. \tag{92}$$

From (1), (91), (91a) and (92) it follows that:

$$\begin{aligned}
i = {} & K_1 e^{-a\eta F/RT} e^{-(\epsilon_r - x)\, a F/RT} \\
& - K_2 e^{(1-a)\eta F/RT}\, e^{(\epsilon_r - x)(1-a) F/RT}.
\end{aligned} \tag{93}$$

If $\eta = 0$, $i = 0$.

Hence,

$$K_1 e^{-(\epsilon_r - x)\, a F/RT} = K_2\, e^{(\epsilon_r - x)(1-a) F/RT} = K. \tag{94}$$

Therefore, from (93) and (94),

$$i = K\left[e^{-a\eta F/RT} - e^{(1-a)\eta F/RT} \right].$$

If η is less than 50 mv., the exponential terms are less than at room temperatures.

Thus,

$$\eta \simeq \frac{RT}{KF}\, i.$$

At limitingly low values of the overpotential, therefore, the overpotential is linearly dependant upon current density, in contrast to the logarithmic dependance at higher values of the overpotential (*i.e.* at higher current densities) when $\overleftarrow{i}$ can be neglected. This result, which is independant of the mechanism assumed, has been experimentally confirmed.

(VII) *Summary*

Which of the above three reactions is the rate determining reaction upon the different metals is not known for all metals owing to the lack of experimental data. On mercury and the metals of high overpotential the adsorption of hydrogen is small, *i.e.* little hydrogen tends to build up upon the electrode surface, so that the slow discharge reaction is probably rate determining. For metals of low overpotential, where the slope of the TAFEL equation is about 0·029 (*e.g.* platinum) the mechanism involves the catalytic

mechanism. For metals of intermediate overpotential, such as nickel, silver, *etc.*, the rate determining reaction is not yet certain because of the lack of knowledge concerning the amount of atomic hydrogen on the surface. Assuming, as appears true for iron for example, that a considerable quantity of adsorbed atomic hydrogen exists upon the electrode surface, the most probable mechanism involves the electrochemical reaction. The above remarks apply to acid solutions. In alkaline solutions the number of hydrogen ions is small and consequently the discharge reaction probably takes place from a water molecule, in place of a hydroxonium ion.

The complexity of some of the experimental results on overpotential indicates the possibility that in some systems a "dual theory" may be applicable, *e.g.*, catalytic and electrochemical mechanisms of desorption may take place at comparable rates. There is also evidence that the mechanism of the hydrogen evolution reaction may change at a given current density, where there is, as for example with platinum at high current densities, a sharp change in the slope of the TAFEL line.

(iv) *The Electrolytic Separation of Hydrogen and Deuterium*

The fact that various electrode materials have different efficiencies in bringing about the electrolytic separation of hydrogen and deuterium, has served to give the hydrogen overpotential on various electrodes a considerable practical importance. It is found that when a mixture of hydrogen and deuterium is electrolysed, the hydrogen is preferentially evolved, thus concentrating the deuterium in the solution. Under appropriate conditions considerable enrichment can be obtained by this method and electrolysis is at present used as the sole method for separating deuterium. The efficiency of the electrolytic separation is measured by the separation factor, s, which is defined by the equation

$$s = \frac{\left[\dfrac{H}{D}\right]_{Gas}}{\left[\dfrac{H}{D}\right]_{Liquid}}.$$

In the equilibrium state, this separation factor, determined by

shaking gaseous mixtures of hydrogen and deuterium with water at high pressure in the presence of active platinum as a catalyst, has a value of approximately 8·8. In electrolysis, the separation factor is considerably greater and it is found that under comparable conditions current density, temperature, state of the surface, electrolyte, *etc.*) the nature of the metal affects the separation factor in the opposite direction to that in which it affects the overpotential. Thus, for metals of low overpotential (*i.e.* "active" electrodes) the separation factor is high and vice versa. At mercury, at which the highest overpotentials are observed, the separation factor has approximately the equilibrium value of 4, and on active metals such as platinum, gold, *etc.*, the separation factors have values of the order of 20.

The increase of the separation factor in electrolysis compared with the equilibrium value is caused, at least for certain of the metals in which the rate determining reaction is slow discharge, by the difference in the activation energies necessary for the transfer of $H_3O^·$ and $H_2DO^·$ ions to a state of adsorption on the metal surface. Thus, for the same quantity of hydrogen and deuterium ions in the solution it follows that the separation factor is approximately given by

$$S = \frac{\dfrac{dc_{H^·}}{dt}}{\dfrac{dc_{D^·}}{dt}} = e^{-(\Delta G_H - \Delta G_D)/kT}. \tag{95}$$

If $\Delta G_H - \Delta G_D$ is placed equal to the experimentally measured difference in the heats of hydration of $H^·$ and $D^·$ (*i.e.* about 1 kilocal), then $S = 5$, *i.e.* the value of the separation factor is approximately that found on inactive metals. A correct order value for the higher separation factors can, however, also be obtained by assuming that the limiting reaction is the catalytic combination of hydrogen atoms, where the difference in the zero point energies of the H and D atoms provides the physical basis for the difference in rates of evolution.

(v) *Cathodic Deposition of Metals*

(1) *Activation overpotential in metal deposition*

As mentioned above, activation overpotential is observed not only in the deposition of gaseous ions but frequently in metal deposition. Overpotential occurring in metal deposition is more affected by the composition of the electrolyte than is hydrogen deposition. For instance, the deposition of lead and mercury from solutions of their nitrates occurs at quite high current densities and is accompanied only by concentration overpotential, whereas deposition of these metals from the acetates involves appreciable activation overpotential as well [1].

A typical example of a current-potential curve obtained in metal deposition is shown in Fig. 70 for the electrolysis of CuCN and KCN solutions at carbon electrodes. Using copper solutions only as the electrolyte, the polarisation is practically all concentration polarisation, but in the presence of cyanide an activation overpotential is observed which rises with increasing cyanide concentration and decreasing temperature. One possible explanation of the latter facts is that the rate controlling reaction is the formation of free $Cu^{\cdot}$ ions from the complex ions $Cu(CN)_2{}'$ and $Cu(CN)_4{}'''$, which are present in the cyanide solution. This view is favoured by the fact that with an alternating current of about 16 cycles/sec., copper electrodes dissolve quickly in potassium cyanide solution;
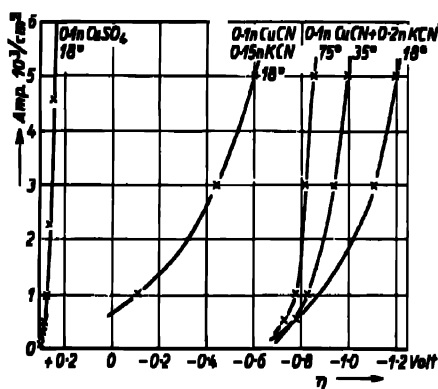
Fig. 70.
Current density-potential relation during the deposition of copper from complex cyanide solutions

but that at higher frequencies (*e.g.* 1000 cycles/sec.) the dissolution has almost completely ceased. Thus, complex formation would be almost complete in $^1/_{16}$ sec. so that the cathodic current pulse can no longer deposit the $Cu^{\cdot}$ ions formed during

[1] A criterion for the absence of concentration polarisation is that the polarisation remains practically unchanged on stirring the electrolyte.

the anodic current pulse. After $1/1000$ second, however, complex formation has not yet begun and it is possible for anodically dissolved copper to be deposited again in the succeeding pulse. In other words, no net dissolution of copper takes place. The formation of the cyanide complex therefore occupies a definite time and the same must be assumed for the dissociation of the complex. The equilibrium constant of the reaction,

$$Cu(CN)_4''' \rightleftharpoons Cu' + 4CN' \qquad (96)$$

has been obtained from e.m.f. measurements on concentration cells (see p. 266), and is

$$K_c \simeq \frac{c_{Cu'} \cdot (c_{CN'})^4}{c_{Cu(CN)_4'''}} = 5 \cdot 10^{-28} .$$

As the equilibrium should be regarded as dynamic it follows that:

$$\frac{d}{dt} c_{Cu'} = k_{dissocn.} \cdot c_{Cu(CN)_4'''} = \frac{d}{dt} c_{Cu(CN)_4'''} = k_{formation} \cdot c_{Cu'} \cdot (c_{CN'})^4 ,$$

and

$$K_c = \frac{k_{dissocn.}}{k_{formation}} ,$$

where the k values are the rate constants of the respective reactions. It therefore follows that the ratio of the time of decomposition of the complex to the time of formation at unit concentration is

$$\frac{dt}{dc_{Cu'}} \bigg/ \frac{dt}{dc_{Cu(CN)_4'''}} = \frac{k_{formation}}{k_{dissocn.}} = \frac{1}{K_c} = 2 \cdot 10^{27} . \qquad (97)$$

If it is taken that the time of formation of the complex is of the order of 10^{-2} sec. from the above alternating current experiments, then the time of decomposition under similar conditions would be of the order of 10^{25} sec., *i.e.* practically infinitely slow. This indicates that the supply of Cu' ions by the decomposition of the complex occurs too slowly to be connected with the deposition process. Similar calculations can be made concerning dehydration of ions as a rate determining process in cathodic deposition and again extremely long times are found to be required for the decomposition of the hydrated complexes into free ions and water.

These results point clearly to the absence of dissociation and dehydration as rate determining reactions. In considering the rate controlling reaction in this case, it might be thought to be a simpler problem than that of the hydrogen overpotential. However, certain special difficulties in the experimental measurement of the metal overpotential, in addition to those met with in the measurement of hydrogen overpotential, retard progress. Thus, the activation overpotential associated with the deposition of metals is usually considerably smaller than that encountered in the evolution of hydrogen. Hence, it is more difficult to distinguish from the accompanying concentration overpotential. A greater activation overpotential is encountered in the deposition of iron, cobalt and nickel than that observed for a number of other ions and this led to the erroneous concept that metals of the iron group had some special property which led to a large activation overpotential during their deposition. More recent measurements have shown that an activation overpotential is associated with the deposition of practically all ions, although there appears to be some tendency for there to be an increase of metal overpotential with increase of work function of the metal. Thus, metals of the platinum group should exhibit higher overpotentials than those shown in the deposition of iron, cobalt and nickel. Hitherto, the electro-deposition of the platinum metals has only been accomplished from complex ions so that comparable measurements have not been possible.

A second special difficulty associated with metal overpotential measurements concerns the change in the electrode surface with time as the deposition takes place. Neglect of this fact led earlier workers empirically to a series of complicated equations for the relation between η and i. More rational results may be obtained if the following two conditions are observed [1]: (i) The metal surface must be a monocrystal. (ii) The overpotential at a given current density must be measured very rapidly after the commencement of the polarising current density.

Thus for the process of discharge across the double layer,

$$v = k_1 a_M \cdot e^{-a e z F/RT} - k_2 e^{(1-a)e z F/RT} , \qquad (98)$$

[1] V. A. ROITER, V. A. YUZA and E. S. POLUYNAN, *J. Phys. Chem. Russ.*, **1939**, **13**, 005, 805.

where k_1 and k_2 are rate constants, and the general form of the equation follows from the more detailed treatment of the kinetics of an ionic discharge mechanism given in the section on hydrogen overpotential. There is no activity term in the second term of (98) because the activity of the pure metal would be involved and this is clearly constant during the discharge. The above equation can be rewritten as

$$v = k_1 a_{\mathrm{M}^\cdot} \cdot \mathrm{e}^{-a\eta z F/RT} \mathrm{e}^{-ae_r z F/RT} - k_2 \mathrm{e}^{(1-a)\eta z F/RT} \, \mathrm{e}^{(1-a)e_r z/FRT} . \quad (99)$$

When $i = 0$, $\eta = 0$ and $e = e_r$. Hence,

$$k_1 a_{\mathrm{M}^\cdot} \cdot \mathrm{e}^{-ae_r z F/RT} = k_2 \mathrm{e}^{(1-a)e_r z F/RT} = i_0 . \quad (100)$$

Therefore,

$$i_{\mathrm{Dis.}} = i_0 \, \mathrm{e}^{-a\eta z F/RT} - i_0 \, \mathrm{e}^{(1-a)\eta z F/RT} , \quad (101)$$

where $i_{\mathrm{Dis.}}$ is the rate of the passage of ions over the energy barrier. It follows from this equation that if i_0 and a could be determined the relation between η and i would be known. These quantities can be obtained from cathode ray oscillographic data upon the velocity of charging of the double layer and the rate of decay of the metal overpotential after the cessation of the polarising current. Thus, for the charging up of the double layer, if i is the net cathodic current, then,

$$\frac{d}{dt} a_{\mathrm{M}^\cdot} = \frac{i}{zF} - i_{\mathrm{Dis.}} , \quad (102)$$

$$= \frac{i}{zF} - i_0 (\mathrm{e}^{-a\eta z F/RT} - \mathrm{e}^{(1-a)\eta z F/RT}), \quad (103)$$

$$= i_0 \left[\frac{i}{zF i_0} - \mathrm{e}^{-a\eta z F/RT} + \mathrm{e}^{(1-a)\eta z F/RT} \right]. \quad (103a)$$

Also, from (41),

$$C = q/e; \quad \therefore \quad dq = C \, de = C \, d\eta . \quad (104)$$

$$\therefore \quad d(a_{\mathrm{M}^\cdot} \cdot zF) = C \, d\eta , \quad (105)$$

$$\therefore \quad \frac{da_{\mathrm{M}^\cdot}}{dt} = \frac{C}{zF} \left(\frac{d\eta}{dt} \right)_1 , \quad (106)$$

$$\therefore \quad \left(\frac{d\eta}{dt} \right)_1 = \frac{zF i_0}{C} \left[\frac{i}{zF i_0} - \mathrm{e}^{-a\eta z F/RT} + \mathrm{e}^{(1-a)\eta z F/RT} \right]. \quad (107)$$

Further, for decay of the overpotential, $i = 0$, so that,

$$\left(\frac{d\eta}{dt}\right)_2 = \frac{zFi_0}{C}\left[-e^{-\alpha\eta zF/RT} + e^{(1-\alpha)\eta zF/RT}\right].\qquad(108)$$

From equations (107) and (108) it is clear that the two unknowns α and i_0 can be obtained, accepting the value of the capacity of an electrode as about $18\,\mu\text{F}$ per sq.cm. of true area (see p. 368).

Determination of the relation between overpotential and current density in this way, *i.e.*, in such a way that measurements are made essentially only of discharge and decay of the potential upon a monocrystalline surface, shows that the TAFEL equation is in fact generally applicable to metal deposition processes except at low current densities, where, as with the electrodeposition of hydrogen, the overpotential becomes proportional to the current density. Typical values of α are $0.4 - 0.5$ and i_0 is about 10^{-13} gram ions per sq.cm./sec. for metals such as iron and nickel and 10^{-10} gram ions per sq.cm./sec for metals such as zinc and copper. As the TAFEL equation can be written in the form $\eta = \dfrac{RT}{F}\ln\dfrac{i}{i_0}$, it can be seen that the activation overpotential associated with the deposition of iron and nickel will be much greater than that associated with the deposition of zinc and copper.

The clarification of the overpotential - current density relation obtained by this method of determination (*i.e.* reduction of vitiating factors in the change of the surfaces of the electrode with time) leads to the acceptance of the most obvious slow step in the deposition of metals, namely that of slow discharge [1, 2].

The detailed mechanism of cathodic metal deposition from complex salt solutions, particularly where the metal is present in the anion as in $Cu(CN)_4'''$, is not known at present. Observations on the speed of growth of various faces of single crystals

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[1] Formerly the variety and complexity of the relations between η and i determined by use of a continuous current led authors to the assumption of several different slow stages controlling the kinetics of metal deposition reactions, *e.g.* the transfer of atoms from the points at which they are deposited to their final lattice positions, and the formation of two and three dimensional nuclei, etc.

[2] See also H. FISCHER, The role of inhibitors in electrolytic metal deposition, *Z. Electrochem.*, 1943, 49, 343, 376.

in the electrolysis of both aqueous solutions and melts show that the adsorption of ions and solvent molecules has an important effect on the deposition process [1].

(II) *Codeposition of two or more cations*

The dependence of overpotential on electrolyte composition makes it possible to choose solutions where deposition of the various metals occurs at widely separated cathode potentials. It is thus possible to make the current-potential curves for two different noble metals so coincident that they are deposited simultaneously or alternatively so far apart that the co-deposition of a less noble metal is prevented. This latter effect can usually be brought about by adding salts which form complexes with one of the metallic ions and cause the concentration of this ion to be greatly reduced, also raising the overpotential for cathodic deposition. If the current-potential curves are such that both metals are deposited simultaneously the proportion of each ionic species deposited may be found from the curves as indicated in Fig. 71. The current yields for metals 1 and 2 are given
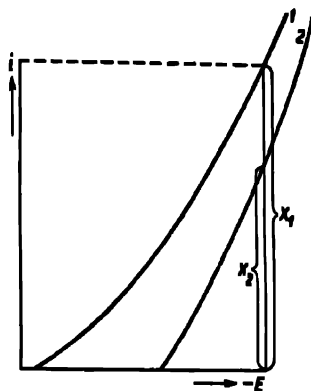
Fig. 71.
Current density-potential curves
in the simultaneous deposition
of metals

respectively by $\dfrac{x_1}{x_1 + x_i}$ and $\dfrac{x_2}{x_1 + x}$, where x_1 and x_2 are the current densities at which the substances 1 and 2 have the same cathode potentials. It can be seen that, owing to the different slopes of the current-potential curves, the proportions of the substances deposited can be varied widely by a suitable choice of current density.

In a similar way the different possibilities of co-deposition of hydrogen and the conditions for the deposition of the metal or the hydrogen alone may be calculated if the appropriate current-potential curves are known. The overpotential of hydrogen at the

[1] M. A. J. WYLLIE, *J. Chem. Phys.*, 1948, **16**, 52.

cathode usually plays an important part in these cases. In general the deposition potential of a cation[1] is (from VII, 49),

$$(e)_{\text{Dep.}} = \eta + e_0 + \frac{RT}{zF} \ln a_{\text{Cation}} \tag{109}$$

and the potential therefore depends not only on the concentration of the ions but also on the magnitude of the overpotential at a given current density, associated with the deposition of that substance. In the case of hydrogen deposition from neutral aqueous solution at 25 °C. ($a_{\text{H}_2\text{O}} \doteq 10^{-7}$), the last term in (109) is —0·41 volt, and therefore

$$(e)_{\text{Dep., H}} = \eta_{\text{H}} - 0 \cdot 41 \ . \tag{110}$$

As η_{H} at many metals has considerable negative values (see p. 423), not only those metals with deposition potentials in neutral solution on the noble side of —0·41 volt can be deposited but even metals such as zinc which are generally classified as base metals. In these cases $(e)_{\text{Dep., H}}$ is more negative than $(e)_{\text{Dep., met.}}$. The existence of the lead accumulator also depends on the high hydrogen overpotential of hydrogen on lead; for were this not large, hydrogen, and not lead, would be deposited as is emphasized by the fact that the hydroxonium ion activity is high in the acid and the lead activity is low owing to the sparing solubility of lead sulphate.

If, however, $(e)_{\text{Dep., H}}$ is more positive than $(e)_{\text{Dep., met.}}$ at a given current density, hydrogen is deposited wholly or predominantly. This is the case for example with the alkali and alkaline earth metals over the whole range of the current-potential curve and no deposition of these metals can take place from aqueous solution. If $(e)_{\text{Dep., H}} \doteq (e)_{\text{Dep., met.}}$, then metal and hydrogen are co-deposited and the current yield of metal deposition is again obtained from the current-potential curves (see Fig. 71). An example is the deposition of iron from neutral solutions, iron having a high overpotential for deposition onto itself comparable in magnitude to that of hydrogen under the same conditions. When hydrogen ions are deposited from the neutral solution the electrolyte in the vicinity of the cathode becomes more alkaline and the ionic product

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[1] See also L. B. ROGERS and A. F. STEHNEY, *J. Electrochem. Soc.*, 1949, **95**, 25.

of ferrous hydroxide is frequently exceeded. Consequently a secondary deposition of hydroxide occurs so that in such cases dark deposits are obtained. A similar example is provided by the deposition of chromium from neutral solution.

A special case arises when the metal to be deposited can form an alloy with the electrode material in the form of a chemical compound or a mixed crystal as for instance has already been encountered in the polarographic analysis of alkali and alkaline earth ions at the dropping mercury electrode (see p. 418). Owing to the considerable affinity of the alkali and alkaline earth metals for mercury the deposition potential of these ions on mercury electrodes is displaced from its normal value by about 1 volt in the positive direction. Although the alkali metals are the most active metals in the pure state, they can therefore be deposited upon mercury electrodes (see p. 412). This deposition is aided by the fact that the hydrogen overpotential on mercury is particularly large and is the basis of the mercury process for the electrolytic production of alkalis. Alkaline earth amalgams can also be prepared by this method, which is best carried out from non-aqueous solvents such as acetone or pyridine.

Depolarisation of metal deposition by alloy formation also sometimes occurs at solid electrodes, e.g. in the case of the deposition of antimony on copper, of zinc on platinum or sodium on lead. This type of depolarisation is not common, however, because at room temperature the velocity of alloy formation and the diffusion velocity of one metal into another is too small. Alloys can be obtained by the electrolysis of aqueous solutions at room temperature, by depositing the metals from a solution of a mixture of the salts, in which an appreciable depolarisation occurs. The best known example of the process is the deposition of zinc and copper alloys in the form of brass from the complex cyanides [1]. In Fig. 72 the current-potential curves are shown for the deposition of the pure metals, and also of brass, from a solution of composition $m/100$ ($CuCN . 2KCN + Zn(CN)_2 . 2KCN$), the composition of which alters with the current density. It can be seen that the

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[1] For recent investigations of the structure of these alloys, see, for example, E. RAUB and A. ANGEL, Z. Electrochem., 1943, 49, 89.
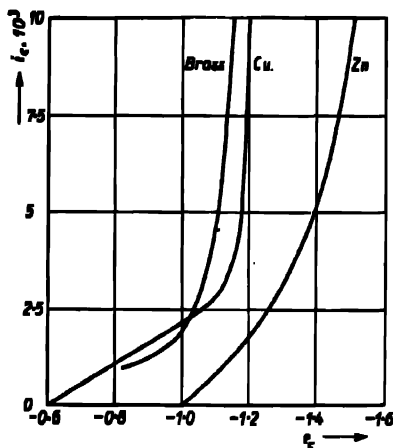
Fig. 72.

Current density-potential curves in the deposition of copper and zinc, or brass, from a solution of cyanide complexes

copper depolarises the process of deposition of zinc by about 0·2 volt, the curve for the deposition of brass being nearly coincident with that for the deposition of copper at low current densities, whilst that for the deposition of pure zinc is considerably displaced to less "noble", i.e. more positive potentials. At higher current densities the deposition of brass occurs at lower potentials than the copper deposition [1]. Brass plating is often used in industry as an intermediate process to facilitate the deposition of adhering metal deposits of one metal upon another. Thus for example, nickel does not deposit well on zinc but good adherent deposits are obtained if the zinc is first brass plated and then coated with nickel.

(vi) *Cathodic Reduction of Inorganic and Organic Substances*

Electrolytic reduction processes (see p. 260) are concerned either with a simple discharge of ions or with a reaction in which hydroxonium ions take part and which results in the oxygen content of the substances undergoing reduction becoming decreased or the hydrogen content becoming increased. The governing factors are similar to those of metal deposition. Whether reduction takes place with or without evolution of hydrogen depends on the form and position of the current-potential curve. Thus, it depends upon the standard electrode potentials (see Tables 24 and 25, p. 262 and 263) and the activities of the substances present; upon the overpotential of hydrogen and the electrode material used, and upon any irreversible polarisation which occurs

[1] See also A. LEVIN and V. SOTNIKOV, *J. Gen. Chem. Russ.*, 1948, 13, 667.

in the reduction process itself. The catalytic activity of the electrode is therefore also of importance.

In some cases reduction of ions takes place practically reversibly (neglecting concentration polarisation) as, for example, in the reduction of $Fe^{...}$ to $Fe^{..}$ at platinum, gold or iridium electrodes. Conversely, the reduction of most polyvalent cations such as $Cr^{...}$, $Mo^{...}$ and $Sn^{....}$ to lower states of oxidation and the reduction of organic substances are usually associated with an appreciable overpotential. The general criterion that irreversible polarisation is present in a given case is that the position of the current-potential curve depends markedly on the nature of the electrode.

Reversible oxidation-reduction reactions (as for iron above) are regarded as proceeding by electron transfer processes, i.e.,

$$Fe^{...} + e_0^- \rightleftarrows Fe^{..} . \tag{111}$$

If the reaction were to take place through the primary deposition of hydrogen according to the scheme

$$\begin{aligned}
H_3O^. + e_0^- &\rightarrow H + H_2O , \\
Fe^{...} + H &\rightarrow Fe^{..} + H^. , \\
H^. + H_2O &\rightarrow H_3O^. , \tag{112}
\end{aligned}$$
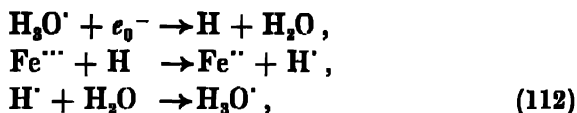
then the reaction would be expected to be accompanied by the hydrogen overpotential appropriate to the metal present. Such is not the case. Furthermore, the above reaction (111) takes place at approximately the same rate in anhydrous pyridine as in water.

In slow reductions and certainly in the cathodic reduction of many uncharged compounds, which almost always requires an overpotential, a primary discharge of hydroxonium ions takes place followed by a reduction by the hydrogen atoms produced. This view is supported by the correspondence between hydrogen overpotential and reduction efficiency at various cathodes. Compounds such as ketones and oximes which are difficult to reduce, undergo reduction only at metals at which the hydrogen overpotential is relatively high (lead, mercury, cadmium, etc.) whilst compounds containing the more easily reducible nitro groups are readily reduced at platinum, copper, or nickel electrodes. Since the hydrogen overpotential can be varied by the choice and treatment of electrode material, it is also possible to control the reducing action of electrodes by making available a potential

range of about 2 volts, corresponding to a range of hydrogen pressure of approximately 10^{34} atmospheres (see p. 240). In addition, at any one cathode the conditions can be closely controlled by varying current density, temperature, pH, and concentration of electrolyte. Much use of the possibilities of reduction control is made in the electrolytic reduction of organic compounds[1]. In the reduction of nitro-benzene to aniline, for example, conditions have been so standardised that all the intermediate products may be prepared in good yield.

The parallelism between electrolytic reduction and hydrogen overpotential is in agreement with the concept that reduction takes place

in so far as the free energy of the hydrogen atoms formed, and hence also their reactivity, increases as the overpotential rises. However, investigations into the reduction of quinone to hydroquinone at platinum electrodes[2] show that this view is certainly untrue in this case. Even at a positive potential of 0·65 volt with respect to the reversible potential the reduction occurs rapidly at smooth platinum electrodes although the velocity of hydrogen deposition at this potential is quite negligible, even at active electrodes. The fact that a smooth platinum electrode can have such different activities for hydrogen and for quinone is hardly in accord with the view that a reduction of quinone occurs through the primary formation of hydrogen atoms. This assumption must also be rejected because the rate of reduction of quinone depends upon the concentration of quinone in the solution, whilst if the reduction involved direct reaction with hydrogen atoms, the discharge of the hydroxonium ions would be rate determining and thus independent of the quinone concentration. It seems likely, therefore, that the rate determining reaction is that between quinone and either one or two hydroxonium ions with simultaneous removal of electrons from the electrode and that this reaction also accounts for the observed overpotential. This concept is supported by the fact that under conditions such that concentration overpotential and

[1] See the list compiled by F. FICHTER, *Organic Electrochemistry*, Dresden and Leipzig, 1942.
[2] See R. ROSENTHAL, A. E. LORCH and L. P. HAMMETT, *J. Am. Chem. Soc.*, 1937, **59**, 1795.

side reactions can be neglected the potential of the electrode during reduction of quinone obeys the TAFEL equation, $\eta = a - b \log i$, and the slope, b, depends markedly on the pH, but is independent of the concentration of quinone. It seems probable, therefore, that here the process of discharge rather than direct reaction with hydrogen atoms, is responsible for cathodic reduction[1].

The cathodic material appears to have a purely catalytic effect upon the velocity of reduction as is indicated by the fact that hydrogen overpotential and reducing action are not always parallel phenomena. For example, the reduction of NO_3' ions to NO_2' takes place on a mercury cathode at a potential 0·6 volt more negative than at platinised platinum, which is attributed purely to the catalytic action of the metal. If it is again assumed that the discharge process is rate determining and that the reduction is not due to a primary hydrogen deposition then this result is still understandable since the "activity" of individual metals for various discharge processes is known to be specific, as is shown, for example, by the different series obtained on classification of metals in order of their oxygen and hydrogen overpotentials.

(vii) *Anodic Dissolution and Deposition Processes*

Two different types of anodic processes are recognized: (a) If the electrode itself takes part in the electro-chemical process this is spoken of as an *anodic dissolution*. Examples are the zinc electrode in the DANIELL cell, the hydrogen electrode in the hydrogen-chlorine cell, and the copper anode used in the refining of copper. These anodes are usually metal electrodes which yield positive ions to the solution. (b) If the electrode material does not undergo anodic dissolution the only electrode process can be the *deposition* of anions (usually hydroxyl or halogen ions) at the electrode. Examples of almost completely insoluble anodes are the noble metals such as platinum and iridium, and to some extent gold, as well as iron and nickel in alkaline solution, and also carbon or graphite. All other electrode materials dis-

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[1] For direct evidence of the absence of reduction of inorganic substances by atomic hydrogen, see V. S. BAGOTSKY and S. A. JOFA, *Compt. rend. Acad. Sci., U.R.S.S.,* 1946, **53**, 439.

solve anodically more or less easily under suitable conditions.

Examples intermediate between these two types of behaviour exist, *i.e.* simultaneous anodic dissolution and deposition of anions may occur. For example, gold dissolves anodically in hydrochloric acid and at the same time chlorine is evolved. In many cases the metal ceases to dissolve on prolonged anodic polarisation and the potential rises until anions are deposited. In such cases the metal is said to have become "passive" (see p. 461).

(viii) *Anodic Dissolution*

At sufficiently small current densities the potential of a dissolving metal corresponds to the equilibrium potential set up between the metal and a solution of its ions at a concentration equal to the instantaneous concentration in the electrolyte. As the current density is raised, however, concentration polarisation sets in as the ions of the freshly dissolved metal accumulate in the vicinity of the anode, thus setting up a concentration gradient. The velocity of ionic diffusion appropriate to the concentration at the anode then controls the anodic phenomena occurring (see p. 402). As the current density is further increased a limiting polarisation value is reached when the solution at the surface of the anode becomes saturated with the metal salt.

Special consideration must be given to those metals which dissolve to give ions of different valencies. An example of this is copper. The standard potentials of this metal with respect to its 2- and 1-valent ions and the standard redox potential for the reaction $Cu^{\cdot} \rightleftarrows Cu^{\cdot\cdot}$ can be obtained from Tables 22 and 24 and have the following values:

$$e_{0,1} (Cu^{\cdot}, Cu^{\cdot\cdot}) + 0 \cdot 159$$
$$e_{0,2} (Cu, Cu^{\cdot\cdot}) + 0 \cdot 345$$
$$e_{0,3} (Cu, Cu^{\cdot}) + 0 \cdot 53 \ .$$

According to thermodynamics, the free energy change accompanying the conversion of 1 g.atom of Cu to $Cu^{\cdot\cdot}$ is the same whether it occurs directly or with the formation of intermediate monovalent ions. Hence,

$$2 \, e_{0,2} F = e_{0,3} F + e_{0,1} F,$$

or

$$e_{0,2} = \frac{e_{0,1} + e_{0,2}}{2} \ . \qquad (113)$$

In general the standard potential for a metal with respect to its ions of higher valency lies between that with respect to its ions of lower valency and the standard potential of the corresponding oxidation-reduction process. Since the reaction $Cu \rightarrow Cu^{\cdot} + e_0^{-}$ requires a more negative potential than $Cu \rightarrow Cu^{\cdot\cdot} + 2e_0^{-}$, copper will go into solution predominantly as the divalent ion. The standard electrode potentials also show that $Cu^{\cdot}$ ions are unstable in aqueous solution and disproportionate according to the equation

$$2\,Cu^{\cdot} \rightleftharpoons Cu^{\cdot\cdot} + Cu \ . \qquad (114)$$

The above reaction moves to the right until the ratio of the ionic activities is such that the electrode potentials of the three processes mentioned above are equal. It then follows that, at 25 °C.,

$$e_1 = 0\cdot159 + 0\cdot059 \log \frac{a^{*}_{Cu^{\cdot\cdot}}}{a^{*}_{Cu^{\cdot}}} = e_2 = 0\cdot345 + \frac{0\cdot059}{2} \cdot \log a^{*}_{Cu^{\cdot\cdot}}$$
$$= e_3 = 0\cdot53 + 0\cdot059 \cdot \log a^{*}_{Cu^{\cdot}} \ , \ (115)$$

where the a^{*} symbols denote the equilibrium activities of the ions involved in reaction (114).

The equilibrium (114) plays an important role in industrial copper refining. As already mentioned a small quantity of $Cu^{\cdot}$ ions is formed along with $Cu^{\cdot\cdot}$ ions until $e_2 = e_3$. From the law of mass action it follows that at a given temperature:

$$\frac{a^{*}_{Cu^{\cdot\cdot}}}{a^{*}_{Cu^{\cdot}}{}^2} = K \ . \qquad (116)$$

In the immediate neighbourhood of the anode the $Cu^{\cdot\cdot}$ activity is higher than that in the bulk of the solution and thus more $Cu^{\cdot}$ ions pass into solution than correspond to equilibrium at some distance from the anode in the bulk of the solution. Consequently, a subsequent decomposition of $Cu^{\cdot}$ ions into metallic copper and $Cu^{\cdot\cdot}$ ions takes place, and the copper deposits as a powder in the form known as anode sludge. The rest of the $Cu^{\cdot}$ ions are also oxidised by atmospheric oxygen in the presence of sulphuric acid, i.e.,

$$2Cu^{\cdot} + \tfrac{1}{2}O_2 + 2H_2O^{\cdot} \rightarrow 2Cu^{\cdot\cdot} + 3H_2O \ , \qquad (117)$$
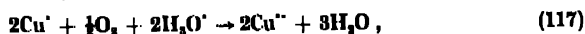
and this leads to a steady consumption of acid. At the cathode the reactions $Cu^{\cdot\cdot} + 2e_0^{-} \rightarrow Cu$, $Cu^{\cdot} + e_0^{-} \rightarrow Cu$, and $Cu^{\cdot\cdot} + e_0^{-} \rightarrow Cu^{\cdot}$ should take place simultaneously because at equilibrium the potentials $(e_0)_1$, $(e_0)_2$ and $(e_0)_3$ are all equal. When the equilibrium is disturbed by reaction (117), a reduction of $Cu^{\cdot\cdot}$ to $Cu^{\cdot}$

occurs at the cathode until a steady state is again reached. It is for this reason that the copper coulometer is unsuitable for precision measurements because not only Cu⁰⁰ ions are deposited at the cathode and apparent deviations from FARADAY's laws ensue. As the temperature rises these deviations increase because equilibrium of (114) is moved further to the right.

Anodic behaviour similar to that of copper is shown by silver, gold and mercury which form the ions $Ag^{\cdot}$ and $Ag^{\cdot\cdot}$, $Au^{\cdot}$ and $Au^{\cdot\cdot\cdot}$, and $Hg^{\cdot\cdot}$ and $Hg_2^{\cdot\cdot}$ respectively. Thus, a mercury anode dissolves at room temperature to the extent of 99·6% in the form of univalent ions, whilst the ratio Hg^{II}/Hg^{I} is independent of the total concentration of mercury ions in the solution and is equal to 285. It follows that the equilibrium between the metal and its ions cannot be formulated as $2Hg^{\cdot} \rightleftarrows Hg + Hg^{\cdot\cdot}$, but rather as $Hg_2^{\cdot\cdot} \rightleftarrows Hg + Hg^{\cdot\cdot}$ and that the univalent mercury ions are diatomic.

The anodic dissolution of mercury is one of the few anodic processes which exhibits little activation overpotential so that only concentration overpotential is observed even at high current densities. Most anodic processes are irreversible just as are the cathodic deposition of hydrogen and of most metals. The accompanying overpotential depends, as in the previously discussed cases, on the current density, the pretreatment of the electrode, the nature of its surface, and the composition of the electrolyte.

Fig. 78. Current density-potential curves for the dissolution and deposition of hydrogen on a number of electrodes

Consider the anodic dissolution of hydrogen which takes place in the hydrogen-chlorine cell. Fig. 78 shows the current-potential curves for the depo-

sition and dissolution of hydrogen at various electrodes. It is seen that the sections of the current-potential curves corresponding for a given electrode respectively to dissolution and deposition are approximately symmetrical. According to (70) and (94) these relations are linear close to the reversilbe potential but at higher current density there is a logarithmic dependence of potential upon current density.

The anodic dissolution of a metal electrode is also usually associated with an overpotential to which the TAFEL equation is applicable. The formation of hydrated ions from metal atoms in the lattice is probably the rate determining process. A particularly large overpotential is associated with the dissolution of nickel, which, in contrast to iron and cobalt, dissolves without becoming passive up to comparatively high current densities. It appears, therefore, that the metal atoms require a considerable activation energy before they can escape their strong attachment to the lattice, and that the magnitude of this activation energy depends on whether the lattice is complete or partly disintegrated. At high current densities nickel anodes become passive and after a considerable rise in potential oxygen is evolved (see p. 464).

(ix) *Anodic Deposition*

(1) *Deposition of chlorine, bromine and hydroxyl ions*

The deposition of chlorine and bromine at inert electrodes (and also their cathodic dissolution on platinum and especially iridium) show curves similar to the curves in **Fig. 73**. The overpotential-current density relations pass linearly through the reversible potential whilst at higher current densities, they pass over to the usual logarithmic relation. The TAFEL equation is valid over part of the curve, but some discrepancies arise with dissolution (as in the case of hydrogen) and these are probably connected with slowness of the reaction $X_2 \rightarrow 2X$. At present the small amount of data available in this field is not at variance with the concept that these anodic phenomena are also explicable from a slow discharge view-point. The deposition of iodine occurs easily on various electrodes; the activation overpotential is negligible, *i.e.* the potentials correspond to the reversible value.

The available experimental evidence for the kinetics of oxygen evolution resulting from the deposition of hydroxyl ions is much less extensive and reliable than that for hydrogen and for metal deposition. A considerable difficulty in the case of oxygen evolution is that of film formation and passivity of the anode material. The results are relatively reproducible on platinum and gold electrodes. In general, the oxygen overpotential is numerically larger than the hydrogen overpotential at the same current density. The TAFEL equation only applies for the phenomena at most metals over a comparatively short current density range and the b value varies between about 0·07 and 0·30.

The theory of the mechanism of the oxygen evolution reaction is likewise much less developed than that of hydrogen. Obvious possible slow stages are somewhat analogous to those discussed with reference to hydrogen, *e.g.*, (i) the neutralisation of OH' ions, or (ii) the combination of adsorbed atomic oxygen. Some information of theoretical interest can be obtained from spectroscopic data, from which it is possible to calculate the standard potential of the OH radical and the oxygen atom at a pressure of one atmosphere. These standard potentials amount respectively to 2·01 and 1·60 volts on the hydrogen scale. As the standard potential of the oxygen electrode is about 0·40 volt, the maximum overpotentials to which these species could give rise would therefore be approximately 1·6 and 1·2 volt respectively. Only the first of these values is sufficient to cover the range of the observed values so that it at first appears that if the slow stage in the anodic reaction is the combination of hydroxyl radicals, the magnitude of the observed overpotential would be explained. Thus the hydroxyl radicals might combine as follows:

$$2OH \rightarrow H_2O + O , \tag{119}$$

$$2O \rightarrow O_2 . \tag{120}$$
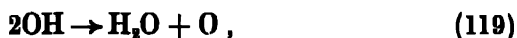
However, an examination of the disappearance of OH radicals in dissociated water vapour indicates that this does not take place to any appreciable extent in the gaseous state, so that it does not seem probable that it would occur at the anode.

In this connection, it is of interest to note that a completely

reversible oxygen electrode can be set up experimentally if oxygen is bubbled through a porous carbon electrode immersed in alkaline solutions of *hydrogen peroxide*[1]. The potential of this reversible oxygen electrode corresponds to the overall reaction

$$O_2 + H_2O + 2e_0^- \rightleftarrows OH' + HO_2' . \tag{121}$$

This reaction involves, in one direction, the discharge of OH' ions so that as the electrode process is reversible it seems that this discharge may be a comparatively rapid process. It is therefore more probable that it is the formation of the HO_2 radicals with which the OH' radical can react which forms the slow stage in the oxygen evolution reaction. This concept is supported by the fact that the addition of small amounts of H_2O_2 to the solution causes a drop in oxygen overpotential.

A possible reaction path at the anode would then be,

$$\begin{aligned}
OH + OH &\rightarrow H_2O_2 . \\
OH + H_2O_2 &\rightarrow H_2O + HO_2 , \\
OH + HO_2 &\rightarrow H_2O + O_2 .
\end{aligned} \tag{122}$$
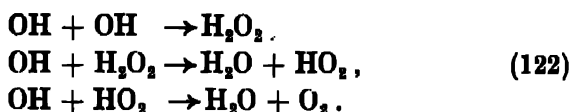
These suggestions[2] are, however, at present speculative.

Apart from oxygen and the halogens, certain other anions undergo electro-deposition. Thus, when alkali sulphides are electrolysed on platinum electrodes in aqueous solution, the formation of polysulphides is first observed and then later, after the solution has sufficiently increased its content of S'' ions, the deposition of elementary sulphur occurs. This, when deposited on the electrode, acts as an insulator and interrupts the current. The sulphur then undergoes slow dissolution as mono-sulphide, and the current strength gradually increases again, so that there occur periodic variations of voltage and current, the frequency of which increases with increasing concentration of sulphide in the solution.

In the electrolysis of alkali or alkaline earth hydrides in the solid state or dissolved in a salt melt, hydrogen is deposited at the *anode* in accordance with FARADAY's Law. Correspondingly, carbon sometimes forms the anion in carbides as does nitrogen in azides.

(II) *Deposition of bisulphate, sulphate and carboxylic acid anions*

The standard potentials of many anions are not known. However, the fact that their deposition potentials on platinum at low current densities must be considerably higher than that of the OH' ion,

[1] W. G. BERL, *Trans. Electrochem. Soc.*, 1943, **83**, 253.

[2] A. HICKLING, *Quart. Rev. of the Chem. Sec.*, 1949, III, No. 2, 95.

follows from the fact that the decomposition potential of most aqueous acid or alkaline solutions has a constant value of 1·70 volts, independent of the nature of the acid or alkali. The same entities are thus discharged independently of the nature of the acid radicals. The only entities present in all aqueous solutions are hydrogen and hydroxyl ions, which must therefore be the ions which discharge at platinum electrodes in acid or alkaline solution.

By using high current densities and electrodes at which the oxygen overpotential is high, it is possible to deposit certain anions simultaneously with, or preferentially to, the hydroxyl ion. This fact is made use of in the industrially important preparation of persalts. If a strong solution of sulphuric acid is electrolysed at smooth platinum electrodes at high current density, HSO_4' and SO_4'' ions are discharged as well as OH' ions and persulphuric acid is produced, according to the reactions:

$$2HSO_4' \rightarrow H_2S_2O_8 + 2e_0^- \quad \text{and} \quad 2SO_4'' \rightarrow S_2O_8'' + 2e_0^-. \quad (123)$$
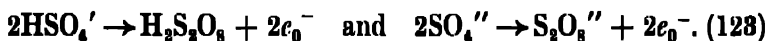
In the presence of $NH_4^{\cdot}$ or $K^{\cdot}$ ions, ammonium or potassium persulphate respectively crystallise out on the anode. When electrodes such as platinized platinum or iridium, which exhibit a smaller oxygen overpotential than smooth platinum, are used, no formation of persulphate occurs. Under suitable conditions (high acid concentration and low temperature) the current yield can be so increased that up to 80% persulphate can be produced. Percarbonates and perphosphates can be prepared by a similar anodic oxidation and these are used like the persulphates in the manufacture of hydrogen peroxide.

A further example of deposition of other anions preferentially to the hydroxyl ion is found in the *Kolbe synthesis*, where the anions of aliphatic carboxylic acids are deposited and form paraffin and olefin hydrocarbons together with some by-products. The electrolysis of neutral or slightly acid acetate solutions at smooth platinum electrodes may be made to yield either ethane at high current densities or mainly methane at low current densities.

The mechanism of this much studied, and until recently not fully understood, reaction has now been elucidated by the introduction of deuterium into, for example, the acetic acid to be electrolysed [1]. At high current densities discharge of anions

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[1] K. CLUSIUS *et al.*, *Z. physikal. Chem.*, 1942, **190** A, 241; 1943, **192**, 273.

takes place almost exlusively and the acetoxyl radical undergoes a secondary exothermic reaction to form CO_2 and a methyl radical, as follows:

$$2CH_3COO \cdot \rightarrow 2CH_3COO + 2e_0^- \rightarrow 2CH_3 + 2CO_2 - 20 \text{ k.cal.} \rightarrow C_2H_6 + 2CO_2. \quad (124)$$
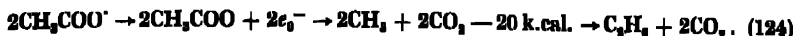
The adsorbed CH_3 radicals are present in such high concentration at high current densities that their combination to ethane occurs very rapidly. The energy released in this process, about 94 k.cal. per mol, is given up to the electrode as in the analogous case of the adsorption of hydrogen. At low current densities the concentration of CH_3 radicals is small and their combination to ethane is less important than their reaction with excess acetic acid according to the equation

$$CH_3 + CH_3COOH \rightarrow CH_4 + -CH_2COOH - 6 \text{ k.cal.} \quad (125)$$

When CH_3COOH in D_2O is electrolysed only CH_4 and *not* CH_3D is formed, and this shows that the fourth H atom of the methane produced originates from the methyl group of acetic acid. The molecular residue $-CH_2COOH$ is transformed completely into CO_2 and H_2O by the oxygen also deposited at low current densities, and as a result the cathodically deposited hydrogen consists at first only of D_2 although later on increasing amounts of H_2 are evolved. The methane, however, always remains free of deuterium.

In the electrolysis of higher fatty acids it is mainly olefines which are evolved at the anode. Thus, propionic acid gives mostly ethylene, besides small amounts of ethane, butane and ethanol. Here again the introduction of deuterium into the acid molecule gives a clear decision on the mechanism of removal of hydrogen from the ethyl radicals by the simultaneously deposited oxygen. If $CD_3 . CH_2 . COOH$ and $CH_3 . CD_2 . COOD$ are electrolysed, the same ethylenic compound $CD_2 = CH_2$ is formed in both cases, and it follows that the hydrogen originates from the methyl group and not from the methylene group of the radicals $CH_3 . CD_2'$ and $CD_2 . CH_2'$; for otherwise, two different ethylenes would be formed differing in molecular weight by two units.

(x) *Electrochemical Oxidation and Substitution*

Anodic oxidation of organic compounds is largely irreversible. As illustrated above in the case of the KOLBE reaction, in the anodic oxidation of organic compounds complete decomposition usually takes place to carbon dioxide and water. Reversible redox systems such as that of hydroquinone-quinone are rare. Although in some cases the oxidising reaction at the anode can be controlled, considerable current and material losses nearly always occur owing to extensive oxidation to resinous materials. Even simple oxidations, such as that of a primary alcohol or aldehyde to a carboxylic acid, do not occur with 100% efficiency because the acid itself undergoes further oxidation. The result

is that in anodic oxidation, — particularly of an aromatic substance, — a multiplicity of products arises and these are usually difficult to separate from each other.

In analogy with the view that cathodic reduction takes place after an initial deposition of hydrogen at the electrode, it has been frequently assumed that anodic oxidation occurs after a primary deposition of oxygen whilst higher metal oxides are supposed to play some part in the processes as oxygen carriers. In the case of the oxidation of hydroquinone, however, (cf. reduction of quinone, p. 264), the mechanism is by means of direct reaction with H_2O molecules with a simultaneous release of electrons to the electrode. The release of charges is probably the rate determining process and can be regarded as the cause of the observed overpotential. It is probable that this type of mechanism is a common one and, contrary to the above stated view, primary deposition of oxygen in anodic oxidation may not occur. It is likely that the latter process takes place by direct reaction of the organic substance with the OH' ions, which would then release an electron to the carrier metal. The electron transfer process would then be rate and potential determining.

The difficulties of direct oxidation of organic compounds have led to the introduction of a technique of adding *inorganic oxygen carriers* to the electrolyte. These carriers act as depolarisers and prevent the anode potential from exceeding a certain value. It is the practice to add metal anions having several valency states which set up a definite oxidation-reduction potential at the inert electrode which is not exceeded during the reaction. The best procedure is to work in two stages, the first anodically oxidising the inorganic salt and the second allowing the oxidised salt to react with the organic compound. In this way a controlled anodic oxidation can be achieved whereas direct anodic oxidation may be too extensive. Typical oxygen carriers used are the salts of manganese, cerium, and chromium. As can be seen from Table 24, p. 262, $Ce^{····}$ ions are especially strong oxidising agents; they can convert anthracene directly to anthraquinone in sulphuric acid solutions. The same is true of chromic acid which is prepared from chromic sulphate by anodic oxidation.

Halogens, or related atomic groups such as the thiocyanogen

group, can, like oxygen, be anodically introduced into organic molecules. The best known industrially important example of this process is the electrochemical preparation of iodoform. An aqueous alcoholic solution of KI, made weakly alkaline with sodium carbonate, is electrolysed at a platinum anode. The iodine initially deposited comes to equilibrium with the OH' ions in the electrolyte according to the reaction

$$I_2 + 2OH' \rightleftarrows I' + IO' + H_2O , \qquad (126)$$
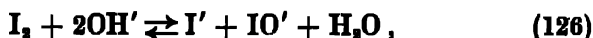
and hypoiodite is formed which oxidises the alcohol to aldehyde, *i.e.*,

$$C_2H_5OH + IO' \rightarrow CH_3CHO + I' + H_2O . \qquad (127)$$

The aldehyde is then attacked by more hypoiodite in stages to form tri-iodoacetaldehyde, thus,

$$CH_3CHO + 3IO' \rightarrow CI_3CHO + 3OH' . \qquad (128)$$

The tri-iodoacetaldehyde is subsequently split up by alkali into iodoform and formic acid, which is itself oxidised by the hypoiodite to carbonate as follows:

$$CI_3CHO + OH' \rightarrow CI_3H + HCOO' , \qquad (129)$$
$$HCOO' + IO' + OH' \rightarrow CO_3'' + I' + H_2O .$$
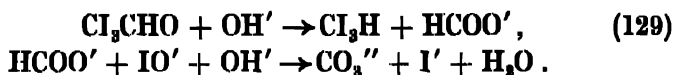
In order to form one mol of iodoform, five mols of hypoiodite are hence required. The net reaction at the anode, obtained by combining (126 - 129) is,

$$3I' + C_2H_5OH + 9OH' \rightarrow CI_3H + 7H_2O + CO_3'' + 10 \, e_0{}^- . \quad (130)$$
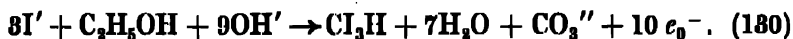
Hydrogen is evolved at the same time at the cathode, *i.e.*,

$$10H_3O^{\cdot} + 10 \, e_0{}^- \rightarrow 10H_2O + 5H_2 , \qquad (131)$$

and the net electrolytic reaction is accordingly

$$3I' + C_2H_5OH + H_3O^{\cdot} + H_2O \rightarrow CI_3H + CO_3'' + 5H_2 . \quad (132)$$
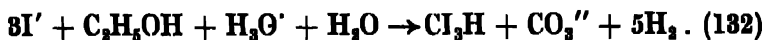
The electrolyte therefore becomes increasingly alkaline as the electrolysis proceeds. In alkaline solution, however, hypoiodite quickly forms iodate, thus,

$$3IO' \rightarrow IO_3' + 2I' , \qquad (133)$$

and the yield of iodoform therefore falls rapidly unless the alkali is continuously neutralised during the electrolysis by passing in carbon dioxide.

In an analogous way, chloral, chloroform and bromoform can be formed. In a suitable solvent aromatic compounds also can be chlorinated. For example, in the electrolysis of a solution of hydrochloric acid and benzene in glacial acetic acid at platinum electrodes a progressive chlorination of benzene takes place. With increase of current density and temperature, chlorination increases up to hexachlorbenzene. As the deposition potentials of oxygen and chlorine at platinum approximate to the same value at low chlorine concentrations, an oxidation frequently occurs as a side reaction producing chlorinated phenols and quinones. Electrochemical halogenation can also be extended to dyestuffs (preparation of eosin and fluoroscein, *etc.*).

(xi) *Electrolytic Methods in Analysis*

Besides polarographic analysis and potentiometric titration methods, several other electrolytic methods of analysis have been introduced and used particularly as rapid techniques. Usually the object of such methods is the successive determination of several metals, *e.g.*, Cu, Zn, Pb, Ni, Cd, *etc.*, rather than the separation of several substances. High current densities and temperatures and rapid stirring of the electrolyte decrease the time for quantitative deposition of each metal.

In the electrolytic separation of several ionic species in the same solution, use is made of the different deposition potentials of the species, or salts are added to the solution which by the formation of complexes causes displacement of the current-potential curves, thus bringing about sufficient difference in their deposition potentials (see p. 448). Two methods are in use, and may be referred to as "outer" and "inner" electrolysis. In the former method the solution is electrolysed by means of an *outer* source of current, usually between platinum electrodes, either at constant current density, at constant potential, or with a variable potential as measured against a reference electrode. This latter measurement is necessary if, for example, the deposition of hydrogen, which

reduces the adhesion of the metal deposits, is to be avoided at the end of the electrolysis when the cathode potential becomes more negative.

In *"inner"* electrolysis a base metal, *e.g.* pure zinc, is used as the anode and this is connected directly to the platinum cathode. A short-circuited cell of the DANIELL type is thereby produced and the ions of the nobler metals in solution deposit onto the cathode. Well defined conditions have to be employed to obtain adherent deposits. The end of electrolysis is detected by a sensitive spot test. If the cathode potential is measured simultaneously against an auxiliary electrode the change in potential shows how much of the metal present has been deposited. According to (VII, 49) in the deposition of copper the cathode potential becomes 0·059/2 volts more negative when the Cu‥ ion concentration is reduced tenfold. The measured change in cathode potential therefore indicates the fractional decrease in concentration of the ion to be determined. For example, if the cathode potential is 0·176 volt at the beginning of electrolysis and has fallen to —0·056 volt when measurements are made then the Cu‥ concentration has decreased by a factor 10^8 (*i.e.*, it has become 10^{-6}% of its original value) and in a typical rapid method of analysis this takes place in about 30 minutes.

Bibliography: A. FRUMKIN, *Faraday Soc. Discussion*, 1947, 1, 57; J. N. AGAR, *Kinetics of Electrode Processes*, Ann. Rep. Chem. Soc., London, 1947, 44, 5; J. O'M. BOCKRIS, *Recent Advances in Hydrogen Overpotential*, Chem. Rev., 1948, 43, 525; A. HICKLING, *The Mechanism of Electrode Processes in Aqueous Solutions*, Quart. Rev. of the Chem. Soc., 1949, III, No. 2, 95; S. FIELD, *Principles of Electrodeposition*, London, 1944; S. GLASSTONE and A. HICKLING, *Electrolytic Oxidation and Reduction*, London, 1936; S. GLASSTONE, *Ann. Rep. of Chem. Soc.*, London, 1937, 34, 110; S. GLASSTONE and A. HICKLING, Chem. Rev., *Electrolytic Oxidation and Reduction*, 1939, 25, 407; H. DIEHL, *Electrochemical Analysis with Graded Cathode Potential Control*, Columbus, 1948.

4. Passivity

A sudden, considerable drop in current may occur whilst a metal is anodically dissolving (see p. 465). Such a phenomenon signifies the onset of the *passive state* of the metal, and in so far

as the metal may no longer be attacked by acid the passivity often remains after polarisation has ceased. In effect the metal has become more noble. If the polarising potential is raised further, oxygen evolution usually begins or in certain cases the metal dissolves to give ions of higher valency than before the voltage was increased.

Two types of passivity are recognised. The first, *mechanical passivity*, depends on the existence of a protective, often insoluble, but comparatively thick and visible, layer (*e.g.* of metal salt) on the metal. This layer virtually isolates the metal from the solution and presents a resistance to the passage of current or causes a large concentration polarisation. *Chemical passivity* [1], on the other hand, occurs without visible change in the appearance of the metal and some of the phenomena connected with it are not as yet explained in full detail.

(i) *Mechanical Passivity*

The protective layer of a sparingly soluble metal salt upon the electrode, which is the fundamental cause of mechanical passivity, is formed in the following way. When the metal dissolves anodically there is an excess of metal ions in the vicinity of the anode. At the same time the solution near the anode loses hydrogen ions owing to the tendency of these to migrate towards the cathode. Continued electrolysis hence causes the solution in the vicinity of the electrode to become saturated with metal ions so that a salt (the normal or the basic salt of the metal, according to the pH of the solution near the anode) tends to precipitate out upon the anode, thus forming an insoluble film, which is, however, *porous*, so that it continues to grow until it is visible.

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[1] The phenomena described here under the term chemical passivity are sometimes discussed under the headings: (i) *Anodic or electrochemical passivity*, which refers to the type of passivity which occurs, for example, in the anodic dissolution of chromium in acid solutions. (ii) *Chemical passivity*, which occurs, for example, when iron is dipped into nitric acid, the initial dissolution being succeeded by a state of passivity in which the iron no longer dissolves. These two subtypes of passivity have been shown to occur for fundamentally the same reasons although they are brought about by respectively electro-chemical and chemical means. They are hence here treated under the heading of chemical passivity.

The effective surface area of the electrode is very considerably decreased in this way, thus giving rise to an increase in current density which in turn brings about a rise in potential so that another process, *e.g.* the discharge of hydroxyl ions, can occur. If the film is a good conductor, *e.g.* lead dioxide, the hydroxyl ion discharge takes place onto the outer surface and oxygen is evolved.

It is characteristic of mechanical passivity that, before the appearance of the protective layer on the metal, the anodic dissolution is approximately reversible, *i.e.*, it occurs near the equilibrium potential, and that the cathodic deposition of the same metal takes place without any marked overpotential. Mechanical passivity, caused by the formation of a film of an insoluble compound on the metal surface, is observed under certain conditions at almost all metals when they are polarised anodically. This is particularly so in alkaline solutions because most metal hydroxides are sparingly soluble in water; they therefore tend to precipitate more easily upon the electrode surface, thus protecting it, *i.e.*, making it passive. A typical example is the anodic behaviour of pure iron in 40% sodium hydroxide at 70 °C. At low current densities the iron dissolves as $Fe^{..}$ ions at a potential of —0·85 volt. When the current density is raised to 0·0088 amp./cm.^{2}, the electrode becomes covered with a black layer of oxide (probably Fe_3O_4) and the potential suddenly jumps to 0·63 volt. After this potential is reached the oxide film becomes brownish red, ferrate ions, $FeO_4^{..}$, are formed, and oxygen is evolved at the same time. The film on the electrode is thus here sufficiently porous to permit further dissolution of iron.

The behaviour is different when the film on the electrode is so adherent and continuous that it almost completely isolates the metal from the solution. If the film also has a low electron affinity the flow of current ceases almost entirely. Potentials large enough for sparks to be observed (up to 1000 volts) can arise in this way. Examples of this behaviour are given by aluminium and tantalum and an oxide film is formed which according to capacity measurements is about 10^{-7} cm thick. The actual protective effect is attributed to an additional gaseous oxygen layer which clings to the electrode partly by adsorption and partly by chemical forces

and almost completely isolates the electrode from the solution.

If the passivated anode is now made a cathode the potential falls because the metal of the electrode yields electrons more easily than do the anions of the solution. The protective layer behaves differently when the direction of current is reversed, and consequently aluminium and tantalum electrodes act as rectifiers, *i.e.*, they allow current to pass in one direction only. Aluminium rectifiers are of restricted use in practice, however, as upon use the oxide film gradually becomes thicker and the ohmic resistance correspondingly increases.

The anodic oxidation of aluminium and its alloys is of great technical importance apart from the use of aluminium as a rectifier. In the Eloxal process, highly protective layers of good insulating power are prepared. Even under ordinary atmospheric conditions aluminium is covered with an adherent and continuous oxide film which accounts for its good resistance to corrosion. By anodic treatment of the aluminium in a suitable solution the oxide film can be made thicker and the corrosion resistance increased. Electrolytes used in the anodising process are sulphuric acid, oxalic acid, or mixtures of these, as well as chromic acid. Depending on the nature of the electrolyte and its concentration, the temperature, the current density and any "addition agents" added to the bath, the anodising process gives protective films of varying colours, hardness, flexibility, conductance and chemical inertness.

(ii) *Chemical Passivity*

If an iron electrode is made anodic in acid or neutral solution the metal dissolves as $Fe^{..}$ ions. If the applied potential is slowly raised a point is reached where the current falls sharply to a very small value, which changes little upon increase of potential. In these respects chromium, cobalt and nickel behave similarly. The anodic dissolution of the metal then virtually ceases and if the applied potential is raised further, oxygen or halogen evolution begins. Similar chemical passivity can be observed in the anodic dissolution of many metals in cells, the e.m.f. of the cells in these cases being lower than the reversible value. The chemically passive

state can also be reached if the metal (iron, nickel, *etc.*) is treated with concentrated nitric acid, chloric acid, or some other oxidising acid. Many metals are also rendered passive by long exposure to atmospheric oxygen.

It is characteristic of chemical passivity that when the applied potential is slowly reduced from a high value the current-potential curve does not trace the same course as it did when the potential was increased. From the behaviour shown in Fig. 74 it may be concluded that chemical passivity causes a permanent change in the state of the metal surface, a concept supported by the fact that a passive metal acts as a noble metal by no longer dissolving in acid. The metal can be reactivated by cathodic polarisation [1], or by bringing it under the solution into contact with a baser metal such as zinc or cadmium. In the latter method the current arising from the short circuited cell which is set up acts in the same way as if the iron were cathodically polarised, so that hydrogen is

Fig. 74. Schematic representation of current density-potential curve for anodic passivity

evolved at the iron (see p. 444). Chemical passivity is found to be favoured by a decrease in hydrogen ion activity in the solution and hence is most liable to occur in alkaline solution. A particular instance is that of nickel which can be used as an inert anode for the decomposition of water in alkaline solution (for example, it is used in the electrolytic gas coulometer). With increase in temperature, passivity occurs less easily and arises only at high current densities. Above a certain critical temperature it appears that metals cannot be passivated.

[1] Passivity can therefore be hindered by superimposing an alternating current of low frequency onto a direct current. The cathodic pulses of the A.C. largely overcome the tendency to passivate. This principle is used in the commercial refining of gold.

The theory of chemical passivity presents many more difficulties than that of mechanical passivity because in the former phenomenon no visible change takes place at the electrode surface, which presents a smooth appearance in both the active and the passive states. Many years ago, FARADAY suggested that chemical passivity was due to the protection of the metal surface by a very thin, invisible layer of metallic oxide, which was supposed to be insoluble in acid. Although the modern theory of chemical passivity is based essentially upon this concept, FARADAY's views have had to be modified and developed for they presented a number of difficulties. Thus, earlier experiments showed that the reflecting powers of a metal in the active and passive states are the same. Further, the oxide layer in FARADAY's view had to be insoluble, whereas oxides such as Fe_3O_4 in the usual form are acid soluble.

These difficulties of the oxide film theory of passivity have more recently been overcome. Thus, it has been shown that polarized light is not reflected in the same way by the active and passive forms of the metal which also have different photoelectric emmission. Secondly, oxides such as Fe_3O_4 are known to be insoluble when in a certain form, *e.g.* after heating. Finally, EVANS showed that by gentle anodic oxidation or by the use of iodine, the metallic part of a passivated metal could be dissolved away, leaving a thin, transparant, but just visible film of oxide [1].

The mechanism of formation of this oxide film occurs in a manner initially similar to that of the formation of the deposit of a salt in mechanical passivity. The porous deposit of normal or basic salt continues to grow until it covers the whole cathode and finally becomes visible. The resultant decrease in area of the metal electrode free for passage of current brings about an increase in current densities and hence a corresponding increase in the electrode potential so that hydroxyl ion discharge occurs, although, contrary to the case of mechanical passivity, this takes place onto the *metal* surface and not onto the deposited layer. An *adherent, invisible* film of oxide is hence formed beneath the comparatively thick layer of salt. When this film of oxide has

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[1] U. R. EVANS, *J. Chem. Soc.*, 1927, 1020.

completely covered the whole of the electrode, surface, oxygen evolution begins, and "blows off" the initial, relatively non-adherent film of basic or normal salt which has served its purpose in decreasing the surface area and thus increasing the current density so that the thin, invisible oxide film could form underneath it. This film remains firmly fixed upon the anode, and in a form not readily attacked by acids. Furthermore, as the metal becomes passive it cannot dissolve, so that no more ions pass through the oxide film. The film cannot grow, therefore, and must always remain invisible.

Confirmation of the above views on passivity has been obtained by an oscillographic study[1] of the cathodic activation of iron passivated in nitric acid from which it was shown that activation consists in the reduction of a surface oxide. With sufficiently short cathodic pulses a quantity of electricity amounting to about 10^{-4} coulombs/cm.^{2}, and independent of the duration of the pulse, was necessary for activation. The value of the product of current density $\times$ time for the removal of passivity was constant even when the time was varied a hundredfold, and this quantity of electricity was found to be sufficient to reduce a monomolecular layer of ferric oxide in accord with the theory outlined above.

If the potential changes associated with passivity on iron in nitric acid are examined in detail with the cathode ray oscillograph it appears that the potential corresponding to the passive state (about $+1$ volt) is displaced by the activating pulse initially to a potential of about $+0.5$ volt. It then falls further independently after the polarising current has ceased to flow and finally reaches the potential of the active state, about $+0.8$ volt. It seems clear that the actual process of activation necessitates the reduction of the monomolecular oxide layer, and this takes place at the intermediate potential of $+0.5$ volt. Local currents then automatically reduce the remainder of the oxide present, and only when all the oxide is reduced does the fall in potential to that of the active state take place. It follows that not all of the oxide present on an electrode is essential for passivity, but that this phenomenom depends upon a monomolecular layer of

[1] K. F. BONHOEFFER and H. BEINERT, Z. *Elektrochem.*, 1941, 47, 147, 441, 580.

oxide having the characteristic properties commented on above.

The oxide film theory of chemical passivity throws light on various experimental facts connected with passivity. Thus, a passivated metal can be activated by making it a cathode because of the reduction of the oxide film consequent upon hydrogen evolution. Passivation often occurs more readily in solutions of higher pH because the oxides of many metals, $e.g.$ iron, cobalt, nickel and chromium are less soluble in alkaline than in acid solution. Finally, ease of passivation decreases with increase of temperature because the solubility of the initial layer of metal salt is increased so that the formation of the visible film is retarded.

The investigations into the passivity of iron are of special interest. If an iron wire passivated in concentrated nitric acid is touched with a zinc rod an active zone appears and this spreads along the length of the wire as is shown by the formation of bubbles. The wire then immediately returns to the passive state due to the nitrous acid produced during the reaction. The spreading of the active area along the wire is in many ways similar to the propagation of a disturbance along a nerve and the activation of a passive iron wire in this way can serve as a model of conduction processes in nerves. The spreading of the activated area takes place when a potential difference exists between an adjacent active and passive spot which then forms a local cell ($cf.$ p. 469) so that a current flows between the "active" anode and "passive" cathode. The latter is reduced and in its turn becomes an "active" anode which will form another local cell with a passive spot further along the wire. This process continues until the area of activation has traversed the whole wire. The initial stimulus is transported along the wire at a rate which, for electrical transport, is comparatively slow, just as is the transport of current along a nerve. Further, in nerve action there is a lower threshold of excitation below which no excitation takes place. This effect has its counterpart in the cathodic activation of iron, for there is a current density below which no activation of the passive metal takes place, even though current may flow for a long time.

Bibliography: U. R. EVANS, *Metallic Corrosion, Passivity and Protection*, London, 1940.

5. Corrosion of Metals

The mechanism of corrosion processes depends essentially upon the action of *"local elements"*. A local cell or element consists essentially of a short circuited voltaic cell having as its electrodes a noble and a base metal dipping into acid solution. Owing mainly to the difference in electron affinities of the two metals of such a cell, one tends to dissolve more rapidly than the other. This dissolution cannot, however, take place unless the supply of electrons liberated by the dissolving metal flows through the conductor connecting the anode to the cathode. It follows that at the latter, more noble metal, hydrogen must be evolved if the dissolution of the baser metal is to continue. In a local cell, therefore, there must be not only electrodes of different electron affinities but also the nobler of these metals must have a comparatively low hydrogen overpotential. The condition for the deposition of hydrogen at a metal is given by

$$e_{\text{Dep.}} = \eta + \frac{RT}{F} \ln a_{\text{H}^{\cdot}} ,$$

where $a_{\text{H}^{\cdot}}$ is the hydrogen ion activity in the solution and η is the total overpotential in the deposition of the hydrogen at a given rate. It follows, therefore, that if a *"local current"* is to flow, the electrode potential of the base metal must be more negative (*i.e.* "higher" in the electrochemical series) than $e_{\text{Dep.}}$. Fundamentally, all corrosion phenomena depend upon this mechanism of the flow of local currents, which leads to the dissolution of the baser component of the local cell.

In practical corroding systems the two electrodes of the typical local cell are the bulk metal (comparatively base, *e.g.* zinc), which undergoes dissolution, and a noble metal of comparatively low hydrogen overpotential, (*e.g.*, copper), which is present in the metal as an impurity. These impurities need not be of a different metallic species from the bulk metal but may be oxides or sulphides of this, having a low hydrogen overpotential. It is hence obvious that the corrosion of very pure metals will be much less rapid than that of impure metals. Local currents (and hence the velocity of corrosion) will be increased

if the difference in the hydrogen overpotential between the two
elements of the local cell is large; conversely, if the noble metal
is, for example, mercury, which has a large hydrogen overpotential,
the corrosion almost entirely ceases. Local currents are also
increased by decrease of the resistance between the poles of
the local element by means of addition of electrolyte to the
solution. In systems out of solution, moisture, *i.e.* water con-
taining a small amount of dissolved electrolyte, has a similar effect.
From the above equation for $e_{\text{Dep.}}$ it can also be seen that re-
duction of a_{H}. causes $e_{\text{Dep.}}$ to become more negative, so that the
condition that $e_{\text{base met.}}$ should be more negative than $e_{\text{Dep.}}$ may
not be maintained and corrosion may cease at a certain pH.
Another important factor in increasing the velocity of corrosion
is the presence of a depolariser (*e.g.* air). This aids the removal
of hydrogen from the cathode of the local cell, and hence increases
the velocity of corrosion. The overpotential of the more noble
metal is now no longer important because the hydrogen can be
removed (and hence the base metal can corrode) by means of the
depolariser even at a surface of large hydrogen overpotential.

A second substance contained in the bulk metal is not always
necessary for the formation of local cells; these can, for example,
be brought about in a metal by strain, which creates areas of different
electron affinities, *i.e.* different electrode potential, so that a po-
tential difference exists between such different areas, giving rise to
local currents and corrosion. Depolarisation by oxygen is neces-
sary here, however, because the difference in the hydrogen over-
potential of the areas of different electron affinities is insufficient
to promote corrosion at an appreciable rate. For example, pure
zinc does not dissolve in dilute acid rapidly until oxygen is
bubbled through the solution.

A different type of corrosion from those described above occurs
when the depolariser (*e.g.* oxygen) is not uniformly distributed
over the metal surface (*differential oxygenation corrosion*). The
parts of the metal which are in good contact with oxygen will
hence undergo more efficient depolarisation than the other parts and
the latter thus become anodic and dissolve, whereupon hydrogen is
deposited at the cathodic regions. This type of corrosion accounts
for the acceleration of the rusting of iron under portions covered

with wet rust; to these oxygen has no access and they therefore become anodic and continue to dissolve whilst oxygen is still available. A similar mechanism is responsible for the corrosion of metals covered by a non metal, *e.g.*, paint.

The above brief outline of the mechanism of corrosion immediately suggests methods for its inhibition. Thus, addition to the solution in contact with the corroding metal of a salt of a noble metal of high hydrogen overpotential, *e.g.* mercury or tin, gives rise to the deposition of the metals and the evolution of hydrogen, together with the corrosion velocity, is very largely reduced. Again, certain organic compounds, mainly aromatic amines such as aniline, acridine and morphine, inhibit corrosion upon addition to the solution. It is found [1] that the inhibition of metal dissolution and the simultaneous increase of the hydrogen overpotential of the dissolving metal run parallel to each other so that the mechanism of inhibition in this case is clearly that the bases of large dipole moment become adsorbed upon the electrode and raise the hydrogen overpotential thereof. In a converse manner, certain substances, *e.g.* nitrobenzene, act as activators because they depolarize the hydrogen deposition at the noble metal inclusions. Similarly, the addition of metals of particularly low overpotential to the solution increases the velocity of corrosion, because of the increased rate at which it is possible to evolve hydrogen upon the deposited additive. Thus, it is a principle of corrosion protection to separate the metal surface from nobler metals of low hydrogen overpotential. For example, if iron is coated with nickel, the iron is only protected from corrosion so long as the nickel completely isolates it from the external cause of corrosion. If the coating is damaged, or if there is a pore, where the iron is exposed, a local cell arises in the presence of moisture, the nickel becoming cathodic and the iron anodic. Because nickel has a comparatively small hydrogen overpotential, relatively large local currents flow and corrosion of the iron is rapid. Conversely, zinc plating of iron is efficacious as a protection, because if the coating is damaged, it is zinc which, being the baser metal, becomes anodic and dissolves, whilst the iron becomes cathodic and is hardly attacked.

[1] J. O'M. BOCKRIS and B. E. CONWAY, *J. Phys. Chem.*, 1949, **53**, 538.

Bibliography: U. R. Evans, *Introduction to metallic Corrosion*, London, 1948; H. H. Uhlig (Editor), *The Corrosion Handbook*, New York, 1948; E. Rabald, *Corrosion Guide*, New York, Amsterdam, 1951.

6. Electrolysis in Melts

The electrolysis of molten salts ("melts") differs in many respects from electrolysis in aqueous solutions. Among the main differences are the high temperatures required, the reactivity of the constituents of the system at high temperatures, the presence of thermoelectric e.m.f.'s and the solubility of metals in melts. The processes occuring during electrolysis both at the electrodes and in the melt itself are not as controllable as in aqueous solution. For instance, in the discussion of FARADAY's laws as applied to melts (see p. 16) it has been seen that the current yield is almost always too small. A frequent cause of these current losses is that the cathodically deposited metals dissolve in the melt, diffuse to the anode and react there with the anodically deposited gases to reform salts. Depending therefore on the solubility of the metal in the melt, the temperature, the current density, the distance apart of the electrodes, *etc.*, the current yields deviate from the theoretical value. Thorough investigations of the electrolysis of lead chloride, for example, have shown that the current yield decreases with increase of temperature, decreasing cathodic current density and decreasing distance between the electrodes, because changing these factors in the direction indicated favours the dissolution of the deposited metal and its transport to the anode [1]. At the boiling point of lead (956 °C.) and at less than a critical current density depending on the experimental conditions, a point is reached where no more lead deposits.

The current yield is dependent on the composition of the melt. Addition of potassium chloride, sodium chloride or barium chloride raises the current yield in the electrolysis of lead chloride, other conditions being unchanged. This finds explanation in the fact that the solubility of lead in these foreign salts is small and falls sharply

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[1] Besides diffusion, thermal convection and stirring by the gas evolved from the anode are important factors.

as the melt becomes increasingly rich in them. Addition of ferric chloride on the other hand decreases the current yield for lead deposition considerably because the reduction of $Fe^{...}$ to $Fe^{..}$ takes place in preference to the deposition of lead.

The losses in current yield caused by recombination of metal and gas deposited at cathode and anode respectively can be reduced by electrolysing at the lowest possible temperature. This can be achieved in practice by working with salt mixtures which melt below the melting point of the pure salt and so choosing the added salts that the solubility of the cathodically deposited metal is depressed. If, in addition, the apparatus is constructed so that the melt is separated into an anolyte and a catholyte and the products of the electrolysis are not allowed to make direct contact, then approximately quantitative yields can be obtained. This is clearly of considerable importance in industrial electrolysis.

A relation of the same type as (109) for the deposition of ions holds also for the electrolysis of melts. The deposition potential depends on the reversible electrode potential and on the over-potential, which in turn depends on the current density. In contrast to aqueous solutions the reversible single potential in melts, measured against an arbitrary zero of potential, is not accurately determinable (see p. 248). It is only possible to measure the e.m.f.'s of cells such as

$$Pb \mid PbCl_2 \mid Cl_2 (C), \qquad (134a)$$
$$\underset{\text{Melt}}{}$$

or

$$Al \mid Al_2O_3 \mid O_2 (Pt), \qquad (134b)$$
$$\underset{\text{Melt}}{}$$
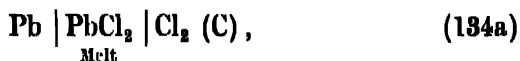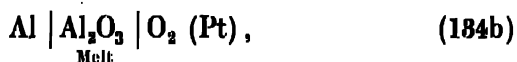
which cannot be separated into single potentials. Here the e.m.f. is a measure of the maximum useful work of the formation of the salt from its elements under given conditions of temperature and pressure. As all the reactants are pure they have an activity of one and hence the electrode potentials are standard potentials. In Table 37 a series of these E_0 values is given for a pressure of one atmosphere together with their temperature coefficients which have been found to be constant throughout the temperature range studied (E_0 is found to be a linear function of T).

It is important in molten salt electrolysis to consider the effect of thermo e.m.f.'s on the measurements. If cathode and anode

are of different materials and a large temperature gradient exists between them, the thermo e.m.f. may constitute a considerable part of the measured e.m.f. [1]

<div align="center">

TABLE 37

THE E.M.F.'S AND TEMPERATURE COEFFICIENTS OF E.M.F. OF CELLS
OF THE TYPE M | MX | X (M')

$$E_t = E_{t_1} - a (t - t_1)$$

</div>

Salt	t_1 °C.	E_{t_1}	$a \cdot 10^4$	Salt	t_1 °C.	E_{t_1}	$a \cdot 10^4$
AlCl$_3$	500	1·997	4·57	PbCl$_2$	500	1·273	6·25
Al$_2$O$_3$	1118	2·215	5·7	PbBr$_2$	450	1·062	6·07
ZnCl$_2$	500	1·573	6·95	PbI$_2$	600	0·54	
ZnBr$_2$	400	1·337	6·8	AgCl	470	0·909	3·0
CdCl$_2$	600	1·325	6·3	AgBr	500	0·787	2·9
CdBr$_2$	580	1·045	7·4	AgI	600	0·528	

An attempt has been made to imitate the procedure in aqueous solutions by evaluating the single potentials of the metals in their melts (i.e. to obtain an electrochemical series for melts) by arbitrarily assuming that one of the single potentials (e.g., II in the cell below) is zero and then making measurements on cells of the DANIELL type,

<div align="center">

Me$_I$ | Me$_I$Cl | Me$_{II}$Cl | Me$_{II}$,   (185)
  Melt   Melt

</div>
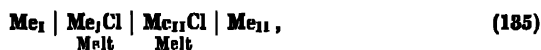
to determine the potential of the other electrode (e.g., I) with respect to this zero. The diffusion potential between the salt melts is, however, not known, and although in some cases this potential is probably small (see p. 279) it is usually so large that any absolute single potentials thus obtained are useless even for approximate calculation [2]. The suggestion has also been made that single potentials of the metals, for example with respect to their molten chlorides, could be calculated from cells of type 184a by taking the potential Ag | AgCl as the arbitrary reference zero. However, this too is unsatisfactory since the chlorine potential varies with different

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[1] For method of correction, see: L. C. CHANG and G. DERGE, Amer. Inst. Min, Met. Eng., Metal Technol., 1946, 13, No. 7.

[2] This can be concluded from the fact that the e.m.f.'s of these DANIELL type cells are not additive. For instance from the e.m.f.'s of the two cells

(Cathode) Pb | PbCl$_2$ | TlCl | Tl (Anode) with $E_1 = 0.398$ volt,

and (Cathode) Cd | CdCl$_2$ | TlCl | Tl (Anode) with $E_2 = 0.315$ volt,

the e.m.f. of the cell (Cathode) Pb | PbCl$_2$ | CdCl$_2$ | Cd (Anode) should be $E_3 = E_1 - E_2 = 0.083$ volt, whereas it is 0.118 volt at the same temperature (650 °C.).

metal chlorides. In addition, little is known of the state of dissociation or activity coefficients of electrolytes in the molten state so that nothing definite can be said about the uncertainties introduced by the variation of the chlorine potential.

Since the reversible single potentials of metals in their salt melts are ambiguous, it is evident that the corresponding deposition potentials are also uncertain. Current-voltage curves are however obtainable for electrolysis of melts and the decomposition potentials can be obtained from these by extrapolation to $i = 0$. In Table 88 some values for the decomposition voltages of various molten salts are given. Special attention must be paid in such measurements to the fact that no depolarisation arises as a result of the dissolution of the deposited metal in the melt and the diffusion of metal to the anode. Such a depolarisation can bring about the flow of a considerable current before the decomposition voltage is reached, and may cause the inflection in the current-potential curve to become less distinct and the extrapolation to $i = 0$ correspondingly less accurate. Another difficulty arises due to the water content of the melt which may cause a spurious inflection in the current-potential curve due to the decomposition of water. The potential applied to the cell then only reaches the value for the decomposition of the salt after the limiting current density (or diffusion current) for water has been attained (see p. 397). Finally, beside the simple decomposition of the salt, other electrode processes may occur. Thus in the electrolysis of molten $SnCl_2$, $SnCl_4$ and not Cl_2 is deposited at the anode, *i.e.* the decomposition potential corresponds to the overall reaction

$$2SnCl_2 \rightarrow SnCl_4 + Sn .$$

Conversely, reduction of the metal to a lower valency state and complete discharge of the metal ions may occur. An example of this is the case of calcium chloride where the decomposition potential corresponds to the net reaction

$$2CaCl_2 \rightarrow 2CaCl + Cl_2 .$$

Special reactions of this kind can be detected by determining the cathodic and anodic current yields.

The decomposition voltages of melts decrease linearly with rising temperature as do the e.m.f.'s of cells such as (184a).

TABLE 38

DECOMPOSITION VOLTAGE OF MOLTEN SALTS FROM CURRENT-POTENTIAL CURVES

Salt	LiCl	NaCl	NaBr	KCl	KBr	KI	MgCl$_2$	CaCl$_2$	BaCl$_2$
t °C.	800	840	800	800	833	842	800	852	1005
Volts	3·17	3·06	2·85	3·10	2·92	2·88	2·49	3·23	3·14

If the electrochemical reaction were to take place reversibly the decomposition voltage would be identical with the e.m.f. of the corresponding reversible cell. However, at the higher current densities, overpotentials are frequently connected with the electrode processes and can be determined by comparing the e.m.f. using the working electrode with that obtained using a stationary auxiliary electrode of the same metal in the vicinity of the cathode. These overpotential values are generally small as would be expected since in aqueous solutions overpotential is known to fall with increasing temperature. The overpotential at constant current density during cationic deposition from molten salts with a common cation depends markedly upon the anion.

Another method of attempting to determine the electrochemical series for the metals in their melts is to determine the cathodic current-potential curves using a calomel reference electrode, the current connection being a glass capillary filled with solid silver bromide [1]. Any diffusion potentials which arise are neglected. A series of potentials is thus obtained which is given in Table 39 and compared with the electrochemical series in aqueous solution. The table shows that the two potential series have several differences as might be expected from previous considerations (see p. 250).

As an example of the difficulties which are often encountered in the field of electrode processes in melts the commercial production of aluminium may be considered. The method is based on the electrolytic decomposition of alumina into aluminium and oxygen. Owing to the high melting point and low electrical

[1] A. DADIEU, *Monatsh. Chem.*, 1926, 47, 207.

TABLE 39

ELECTROCHEMICAL SERIES OF METALS IN AQUEOUS SOLUTION AND IN MOLTEN SALTS

Aqueous soln.	Zn	Fe	Cd	Tl	Co	Ni	Sn	Pb	Sb	Bi	Ag	Hg	
Molten Salt	Al	Zn	Cd	Pb	Fe	Cu	Ag	Sn	Co	Ni	Hg	Sb	Bi

conductance of alumina, molten cryolite, Na_3AlF_6, is used as a solvent. The conductance of molten cryolite-alumina solutions decreases linearly with the alumina content. Extrapolation to 100% alumina shows that the conductance of alumina in the mixed melt is negligible, and transport measurements show that the current is carried mainly by the sodium ions in the melt.

As alumina does not conduct in the melt it was at first assumed that the primary process in the electrolysis of the mixed melt is the decomposition of sodium fluoride into its elements. The alumina was supposed to act as a depolariser both at the cathode and the anode by means of secondary reactions as follows:

Cathodic process, $6Na^+ + 6\,e_0^- \rightarrow 6Na$,

$$6Na + Al_2O_3 \rightarrow 3Na_2O + 2Al \; ; \qquad (136)$$

Anodic process, $6F^- \rightarrow 3F_2 + 6\,e_0^-$,

$$3F_2 + Al_2O_3 \rightarrow 2\,AlF_3 + 3/2\,O_2 \; ; \qquad (137)$$
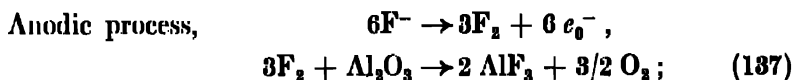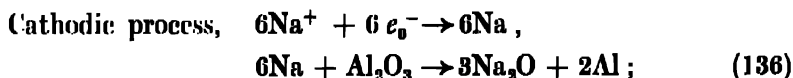
After the further reaction:

$$2AlF_3 + 3Na_2O \rightarrow Al_2O_3 + 6NaF \; , \qquad (138)$$

alumina and sodium fluoride should remain. If the anode is not platinum but carbon the oxygen produced in (137) reacts to form carbon dioxide and carbon monoxide thus giving rise to further depolarisation.

Measurement of the decomposition potentials of cryolite-alumina melts appeared to confirm these suggested reactions. At low current densities the decomposition potentials were found to be 2·10 volts with a platinum anode and 0·98 volt with carbon, whilst the decomposition potential of pure sodium fluoride is calculated thermodynamically to be about 4·5 volts. At high current densities

the current-potential curve rises sharply and as it becomes a logarithmic relation the fact that some electrode process is slower than the others is indicated (see p. 426). Referring to the reaction scheme given above this slow process would be the diffusion of alumina to the electrodes which makes the reactions (186) and (187) proceed at a decreasing rate. If the melt is allowed to solidify the decomposition potential rises to 4·18 volts (or close to that calculated for pure sodium fluoride) because transport of alumina then becomes practically impossible.

However, a more thorough examination of the system [1] has now shown that the mechanism of electrolysis actually differs from the above scheme. It has been established that aluminium reacts vigorously with pure molten cryolite at 1000 °C. with evolution of sodium vapour which burns on the surface of the melt. The melt then contains excess aluminium fluoride after this reaction, in which part of the metallic aluminium disappears, *i.e.*,

$$Na_3AlF_6 + Al \rightarrow 2AlF_3 + Na .   (189)$$

It follows that under the conditions of electrolysis sodium is more noble than aluminium, *i.e.* the secondary reaction (186) cannot occur and aluminium itself must be primarily deposited. The fact that the nobler sodium is not deposited can only be accounted for by the existence of an overpotential for sodium deposition on aluminium. In fact, with a carbon cathode, sodium is preferentially deposited from the melt, but if the bottom of the crucible is first covered with molten aluminium the deposition of sodium is greatly retarded. The co-deposition of sodium and aluminium probably accounts for low current yields in aluminium production; these cannot be explained upon the basis of aluminium metal fogs which are absent from the melt owing to the reaction with the melt to form sodium.

The assumption contained in (187) that fluorine is primarily deposited at the anode and that this gives rise to a secondary evolution of oxygen is an improbable one; fluorine is too electronegative for deposition; *e.g.*, it cannot be deposited from aqueous solution. If fluorine were the primary deposition product as in

[1] E. GRÜNERT. Z. *Elektrochem.*, 1942, 48, 393.

(187) it would be expected to react with the carbon anode to form carbon tetrafluoride, in addition to the products formed by the reaction of the secondarily produced oxygen with carbon. In any case it would be expected that at higher current densities fluorine as well as oxygen would be present in the anodically deposited gas. Under actual operating conditions, however, the electrolysis causes the appearance of only carbon dioxide and carbon monoxide at the anode, and it thus appears that oxygen, or in any case ions containing oxygen, must be primarily deposited. The existence of oxyfluoride complexes, formed when the alumina is dissolved in the cyrolite, can be proved by examination of the solid mixed crystals of alumina and cryolite.

Bibliography: P. Dnossbach, *The Electrochemistry of Molten Salts*, Berlin, 1938; J. O'M. Bockris and J. W. Tomlinson, *Constitution of Melts, Research*, 1949, **2**, 362.

7. Fuel Cells

(i) *Introduction*

Usual methods of producing electrical energy involve the combustion of coal, the production of steam and its use to drive dynamos. Apart from energy losses in the heat of combustion of coal, *etc.*, it is intrinsically impossible to exceed a certain efficiency for the whole process because the conversion of thermal energy into kinetic energy by a heat engine is known to have a maximum possible efficiency given by (II, 98). In practice, the maximum obtainable overall efficiency of the coal-steam-dynamo method is about 30%. Essentially similar remarks apply to modifications of this method for producing electrical energy which involve diesel engines, gas turbines, *etc.* To attain to a less wasteful method of producing electrical energy, a method must be found which avoids the use of a heat engine.

The use of a primary cell would satisfy this requirement and be in principle an extremely efficient method of obtaining electrical energy. In the ideal case, where the cell would function as a source of e.m.f. without the setting up of appreciable polarisation, the efficiency would be 100%, *i.e.* all the energy of the chemical

reaction occurring in the cell would be converted into chemical energy. Most primary cells used in practice involve some metal such as zinc; however, considerable energy is needed to produce the metal from its ores in the first place and when this is taken into account, the net efficiency of the production of electricity from a primary cell is small. What is required, therefore, is this: a primary cell in which the attackable electrode material is one of the substances used as fuels, *i.e.*, essentially, carbon. (As shown below, a secondary fuel obtained from a carbonaceous fuel with only a small energy loss, may also be used). The other electrode material in such a primary cell would be essentially oxygen. Then, in the working of such a cell, the overall reaction is the combination of carbon and oxygen to form carbon monoxide and carbon dioxide; thus, the cell reaction is essentially the same as that occurring in the combustion of fuels, but, in principle, the efficiency of the process should be much greater than that in which electrical energy is produced by a process involving thermal combustion and a heat engine. Cells of the type just described are termed fuel cells. Many fuel cells can be represented in general as:

$$\text{Fuel} \mid \text{Electrolyte} \mid \text{Oxygen (as air)}.$$
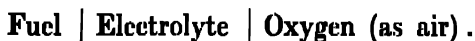
The basic mode of action of all fuel cells is that in which oxygen is applied to the fuel in the ionised state; a potential difference is thus produced between the electrodes and a current flows. Two main types of fuel cells exist. In the *direct* fuel cells carbonaceous matter forms the attackable electrode, *e.g.*,

$$\text{C} \mid \underset{\text{borax, KF and cryolite}}{\text{Melt of } K_2CO_3,\ Na_2CO_3} \mid (O_2)\ \text{Ag}.$$
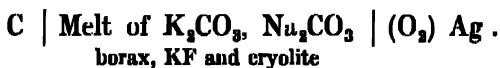
In the indirect fuel cell, gaseous fuels such as hydrogen and carbon monoxide are used to saturate the electrode, *e.g.*,

$$\underset{\substack{\text{sat.}\\ \text{CO}}}{\text{Ni}} \mid \underset{\text{borax}}{\text{Molten}} \mid (O_2)\ \text{Ag}.$$

The reason why the use of fuel cells as a method of producing current is not yet practicable on a large scale lies in the severe practical difficulties associated with them. Thus, the e.m.f. of such cells is small (of the order of 1 volt), so that the cell must

be able to produce a high current strength. This usually sets up polarisation and the current strength drops considerably. To reduce the polarisation sufficiently it is frequent to work at fairly high temperatures (*e.g.* 500 °C., where the use of a molten salt electrolyte is essential). A second difficulty concerns the internal resistance of the cell. This may increase with time owing to the resistance set up by products of irreversible side reactions.

(ii) *Practical Examples of Fuel Cells*

In the *direct fuel cell*, oxygen in the form of some oxygenated ion is discharged at the anode and combines with carbon present there. Electrolytes used for oxygen transport are alkalis such as caustic soda, or acids such as sulphuric acid, as in the cell

$$\text{C} \mid \text{H}_2\text{SO}_4 \mid \text{KClO}_3 \mid \text{C}.$$

Carbonate and lead oxide melts have been used as electrolyte. In a cell utilising fused sodium carbonate, a magnesia diaphragm is used to keep the ferric oxide electrode dry. In this cell, the carbon is attacked by the carbonate according to the equation

$$\text{Na}_2\text{CO}_3 + 2\text{C} \rightarrow (2\text{Na}) \text{ gas} + 3\text{CO},$$

Fig. 75.
Fuel cell with electrolytic solid conductor

giving rise to a high potential, 2 v. After a short time, however, the carbon deposition equilibrium is set up $(2\text{CO} \rightarrow \text{CO}_2 + \text{C})$ and the carbon dioxide brings about oxidation of the sodium vapour, which is equivalent to reduction in the e.m.f.

Solid electrolytic conductors have been efficaciously used in some recent cells [1]; they make possible the use of high temperatures whilst diminishing the corresponding attack on the refractories. The solid electrolyte acts as a diaphragm in separating the carbon anode from an iron oxide cathode, *i.e.*,

[1] E. BAUR and H. PREIS, Z. *Elektrochem.*, 1937, **43**, 727; 1938, **44**, 695.

$$C \mid \text{Solid conductor} \mid (O_2) \, Fe_3O_4$$

(see *Fig. 75*). It is clearly important that the conductor has a small internal resistance and is free from polarisation. Good results have been obtained from a mixture of tungstic oxide (WO_3) and CeO_2 in a ratio of three to one and bonded with clay. The internal resistance is of the order of 1 ohm.

Cells such as the above become heated to the required temperature by virtue of their inner resistance, the efficiency being about 70%, or about double the efficiency of the ordinary heat engine. The most important property of this simple, robust cell is that it is practically perfectly unpolarisable almost to the point of short circuit. This is illustrated in Fig. 76, where the net current from an element containing 5 cells in series is shown as a function of time with different loads. Such an apparatus would produce about 8 kilowatt/m.², which compares well with the space needed in the production of power by coal.
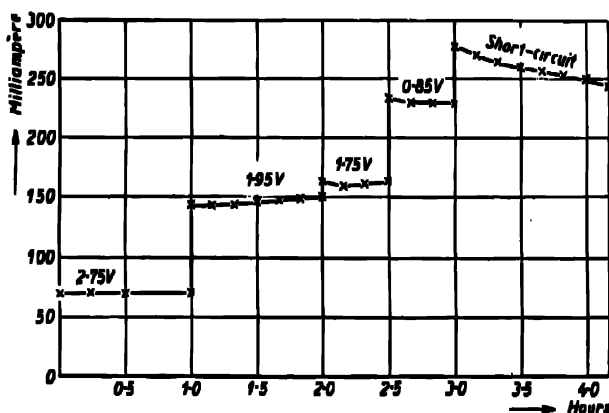
Fig. 76. Current delivered by fuel cells at different load

In the *indirect fuel cell*, gases derived from fuel, *e.g.* CO, are caused to interact in the anode compartment of the cell with discharging oxygen ions. This method has the general advantage that it avoids the removal of ash and the problems relating to the poor ionisation of carbon. Conversely the free energy available for conversion to electrical energy is less than for the combustion of carbon dioxide.

The gases are only effective when in contact with dry electrodes; hence the electrolyte must not wet the exposed position of the tube. It is desirable to attain equilibrium between the adsorbed and free gases as rapidly as possible; in some arrangements this purpose is aided by the use of diffusion electrodes which consist, for example, of porous carbon tubes, the section in contact with the electrolyte being platinized. The gas passes from inside the electrode through its porous walls and can thus become electro-motively active over the whole metal.

Gases used in indirect fuel cells have been most usually carbon monoxide and hydrogen. Attempts to set up carbon monoxide cells to work at room temperature, *e.g.*

$$Cu \mid Cu_2Cl_2 \text{ in acid solution} \mid CuCl_2 \text{ in acid solution} \mid Cu$$
$$\qquad\quad \text{satd. by CO} \qquad\qquad\qquad \text{oxidised by air}$$
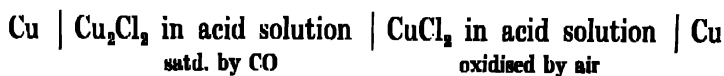
have not been fully successful because there is never a reversible oxidation of carbon monoxide to carbon dioxide.

In a typical high temperature indirect fuel cell, the electrode is usually in the form of an oxide and this undergoes reduction by the fuel gases and becomes subsequently reoxidised by the discharged oxygen. For example,

$$Fe \mid FeO \text{ (Fuel, gas)} \mid Carbonate \text{ melt} \mid Fe_2O_3 \text{ (Fe}_3O_4) \text{ (O}_2) \,.$$

In this cell magnesia was used to prevent wetting of the electrodes; the anode was of iron wire clippings and the cathode of granular magnetite, both contained in porous magnesia blocks. The cathode was kept oxidised by a stream of air and the anode was reduced by hydrogen or carbon monoxide. The temperature of operation was between 900 and 800 °C. and the current density of the order of 1 amp./cm.^{2}.

It will be realised that could a satisfactory fuel cell be produced economically, a new era of the production of power would commence. Much further investigations is necessary, however, before practical difficulties are overcome so that cells can be produced sufficiently cheaply.

Bibliography: H. C. Howard, *Chemistry and Coal Utilisation*, Vol. 2, Chap. 35, p. 1568, New York 1945; J. H. McKee and A. M. Adams, *Fuel*, 1949, **28**, 1; H. J. T. Ellingham, *cf.* Summary in *Nature*, 1950, **166**, 160.

ELECTROCHEMISTRY OF GASES

1. Production of Charge Carriers

(i) *Introduction*

Under normal conditions of pressure and temperature, gases contain virtually no free ions or electrons and are therefore non-conductors. Passage of a sustained current in a gas is possible only if charge carriers (ions or electrons) are produced continuously by some artificial means, the conduction of electricity then being taken over by these charge carriers under the influence of an applied field. Ionisation in a gas may take place either by the absorption of radiation by neutral molecules or by means of transfer of kinetic energy to such molecules during an inelastic collision. Particles of high kinetic energy suitable for imparting energy in such collisions are contained in the α and β radiation from radioactive substances; they can also be produced thermally or by the acceleration of electrons or ions already present in an applied

TABLE 40

IONISATION ENERGIES OF IMPORTANT GASES IN ELECTRON VOLTS

Rare gases		Metal vapour		Molecules			
He	24·48	Li	5·37	H_2	15·8	CO	14·1
Ne	21·47	Na	5·19	N_2	15·7	CO_2	14·4
Ar	15·68	K	4·32	O_2	12·5	NO	9·5
Kr	13·94	Rb	4·19	H_2O	12·7	NO_2	11·0
Xe	12·08	Cs	3·86	Cl_2	13·2	CH_4	14·5
		Zn	9·37	HCl	13·8	C_2H_2	11·3
		Cd	8·94	I_2	9·7	C_6H_6	9·2
		Hg	10·41	NH_3	11·2	HCN	14·8
		Tl	6·08				

electric field. This collision method is the most important one for bringing about ionisation in gases.

For ionisation to take place, the energy, U, transferred in the collision, or obtained from the radiation incident upon the gas, must be at least as great as the ionisation energy, I, of the atoms or molecules concerned, *i.e. the essential condition for ionisation* is

$$U \geq I .\qquad(1)$$

The ionisation energies in electron volts of the more important gases are given in Table 40 (see also Table II, 8 in Chapter XIV).

The condition $U \geq I$ is a necessary but not sufficient one for ionisation since even if it is fulfilled such a collision or absorption process does not always lead to ionisation, because the rate of ion formation depends also on the ionisation probability which in turn depends on the magnitude of U. For $U < I$ it is zero, it then increases with increasing values of U and attains values of about 0·8 for large values of U. [1]

In ionisation processes depending upon absorption of radiation, the condition

$$U = h\nu \geq I\qquad(2)$$

is applicable, where $h\nu$ is the energy of the photon. From this equation and the use of the appropriate numerical values from Tables I, 2 and I, 3 of Chapter XIV, it is possible to evaluate the long wave length limit at which ionisation can occur for any given atom or molecule, namely,

$$\lambda_0 = \frac{h \cdot c}{I} = \frac{12{,}390}{I} \, \text{Å} ,\qquad(3)$$

where I is in e.v. By substituting some I values from Table 40 in (3) it may be seen that radiation of very short wavelengths must be used to bring about ionisation (*e.g.* for Hg, $\lambda_0 = 1190$ Å). If the energy of the photon is greater than I, the difference in energy is taken up as the kinetic energy of the emitted electron. If X-rays (where λ_0 is of the order of 1 Å) are used, the energy $h\nu$ is about 10^3 times larger than I so that the energy of the electron

[1] This refers to ionisation by collision with electrons. In ionisation by collision with positive ions the yield is much smaller because in collisions between masses of the same order there is a considerable transfer of translational energy so that only a fraction of the kinetic energy is available for the ionisation.

produced upon ionisation of a molecule is hence very large and the electron can then give rise to the collisional ionisation of further atoms or molecules until its velocity is greatly reduced. The ionisation of molecules is sometimes accompanied by decomposition, typical processes being the following:

$$CO_2 \rightarrow CO + O^+ + e_0^- \quad (I = 19 \cdot 6 \text{ e.volt});$$
$$NO \rightarrow N^+ + O \quad + e_0^- \quad (I = 22 \quad \text{e.volt});$$
$$H_2O \rightarrow OH + H^+ + e_0^- \quad (I = 18 \cdot 9 \text{ e.volt}), etc. \quad (4)$$
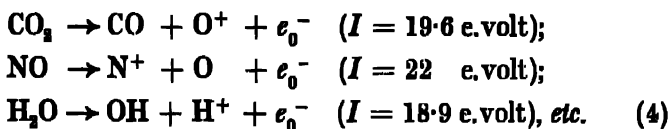
(ii) *The Theory of the Formation of Charge Carriers*

The theory of the *formation of charge carriers by electron impact* in a *homogeneous* electric field can be considered in terms of the *simplest case* in which the primary electrons are formed at the cathode only (*e.g.* by the photoelectric effect). Let N_0 be the number of electrons released per unit area per second at the cathode, and let each primary electron produce a secondary electrons per unit length of its path[1] towards the anode (a is called TOWNSEND's first coefficient), then at distance x from the cathode $N_x = N_0 + N$ is the total number of electrons crossing unit area of the tube. Between x and $x + dx$ it follows that a further

$$dN = N \cdot a \cdot dx \quad (5)$$

electrons are produced since the secondary electrons themselves form new tertiary electrons by collision and so on ("electron avalanche"). Integrating between $x = 0$ and $x = r$ (r = distance between electrodes) the total number of electrons, N_r, arriving per sq.cm. per second at the anode is

$$N_r = N_0 \cdot e^{ar} \cdot \quad (6)$$

Hence, the current density is

$$i = N_0 e_0 \cdot e^{ar} \cdot \quad (7)$$

Collisional ionisation thus effects amplification of the current density by a factor

$$f = \frac{N_0 e_0 \cdot e^{ar}}{N_0 e_0} = e^{ar} \cdot \quad (8)$$

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[1] Ionisation by positive ions is neglected in comparison with that by electrons for the reason stated in the footnote on page 485.

If the field is inhomogeneous, which is practically always the case (see p. 498), then a is a function of x, and hence in place of (8) one obtains

$$f = e^{\int_0^r a \, dx} \tag{8a}$$

The coefficient a must be proportional to the number of collisions per cm. with molecules and hence to the pressure of the gas. It must also depend on the kinetic energy attained by the electrons between two successive impacts. This energy is directly proportional to the product of the field strength and mean free path, and the latter is inversely proportional to the pressure. Consequently, a is proportional to $p \, f(F/p)$ where f represents "function of". Empirically, the dependence of the TOWNSEND coefficient on pressure and field strength is given by the approximate relation

$$\frac{a}{p} = A \cdot e^{-B \cdot p/F}, \tag{9}$$

where A and B are constants, characteristic of the given gas.

The *thermal production of charge carriers*, e.g. that observed in flames, takes place by virtue of the increased energy of the collisions between atoms and molecules themselves. The ions and electrons produced thereby are in temperature equilibrium and hence possess a mean translational energy of $^3/_2 \, kT$, which thus increases with increasing temperature. These ions and electrons can themselves cause further ionisation and are more efficient in bringing this about than are neutral atoms or molecules. The density of the ions would hence increase indefinitely were it not for the fact that they undergo recombination to form molecules again so that a certain temperature dependent equilibrium concentration of ions is set up. For the simplest case of a monatomic gas, and neglecting the energy used by the electrons in giving rise to excited energy states in particles after collision, this equilibrium can be evaluated by means of ordinary chemical kinetics. By equating the rates of formation and recombination, the appropriate calculation leads to the SAHA formula, namely,

$$\frac{a_1^2}{1 - a_1} \cdot p = \frac{(2 \pi m)^{3/2} e^{5/2}}{h^3} \cdot (kT)^{5/2} \cdot e^{-I/kT}, \tag{10}$$

where a_1, is the degree of ionisation of the gas, p is the gas pressure, T the temperature, I the ionisation energy, m the mass of the electron, k the BOLTZMANN constant and h PLANCK's constant.

The equation can be tested by means of conductance measurements on flames and has been shown to be a good approximation. The larger the ionisation energy I, the higher must be the temperature needed to reach a given degree of ionisation. Large degrees of ionisation are only reached at temperatures of several thousand degrees, which in practice nearly always means in an electric arc (see p. 496).

It is also possible to produce charge carriers at the surface of solids, resulting in a continuous current in the gas in contact with this surface. In most cases, this method involves electron emission by heating electronic conductors (*e.g.* metals, metallic oxides, nitrides, *etc.*) so that the electrons which they contain are raised in energy above the level of the thermionic work function of the solid, and are therefore released. As the temperature is raised the velocity of the conduction electrons becomes greater, so that the fraction of them with sufficient kinetic energy to escape is considerably increased. From a knowledge of the energy distribution in the electron gas it is possible to calculate the density of the thermionic current, which is given by

$$i = A \cdot T^2 \cdot e^{-\varphi/kT} \tag{11}$$

(RICHARDSON's equation). The work function of the substance concerned is represented by φ and A is a constant, which varies between 65 and 100 amps/sq.cm. degree^2 for pure metals. Thermionic emission from heated cathodes can thus lead to the passage of quite large currents (as required in radio valves, rectifiers, *etc*).

Solids can also be made to emit electrons by means of incident short wave radiation, the electrons being activated to the energy necessary for escape by the energy of the light quanta (photoelectric effect). Secondary electron emission also results from the impact of ions or electrons on a metal surface. Lastly, some metal salts, raised, to high temperatures, also emit positive ions. For instance, an anode of Fe_2O_3, Al_2O_3 and alkali oxides emits positive alkali ions.

2. Non Self-Sustaining Conduction in Gases

Gaseous discharges which need continuous activation from some external energy source for their maintenance, *e.g.* by means of radiation (photoelectric effect) or thermionic emission, are grouped together as "non self-sustaining discharges". In contrast to this, in the "self-sustaining discharge", the charge carriers are maintained (after their *initial* production by one of the sources mentioned above) in the gas or at the cathode by mechanisms produced by the applied field itself.

The simplest example of a non self-sustaining discharge is pure electronic conduction in a high vacuum. The electrons, which are here the charge carriers, are initially produced at the cathode by irradiation (vacuum photocell), or thermionically and then accelerated towards the anode by means of an applied electric field. In gases, non self-sustaining discharge takes place when the gas is continuously ionised by some external means, such as X-rays or radioactive radiation, and when the field strength and the temperature are too low for collisional ionisation (which would lead to a self-sustaining current) to occur.

The current-voltage curve in such a non self-sustaining current is somewhat analogous to that of the diffusion current in electrolysis (see Fig. 62). There is an initial proportionality between current and voltage, *i.e.* Ohm's law is applicable. This indicates that no new charge carriers are formed by the electric field (see p. 84). The charge carriers move as if experiencing frictional forces, as in the migration of ions in solution, so that a constant applied field gives rise to a constant velocity. At higher applied potentials, the current increases more slowly than corresponds to Ohm's law, and finally a saturation current is obtained, due to the limited number of charge carriers present.

The charge carriers present consist of positive and negative (mostly univalent) ions, and their mobility in, say, air at a pressure of 1 atmosphere and room temperature, is of the order of 1·3 - 1·9 cm./sec. [1]. The ionic radii estimated from this are 3 - 5

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[1] The ratio u_-/u_+ is about 1·88 under these conditions. The negative ions thus always have the greater mobilities and the greater diffusion coefficients.

times as large as the molecular radii. The charge carriers therefore probably consist of complex ions formed by the attachment of water molecules or other, similar dipoles present in the gas, to the original simple ions. Charge carriers having both considerably smaller and greater mobilities than those mentioned above are also observed as, for example, colloidal particles (aerosols) and electrons, respectively.

The magnitude of the saturation current in non self-sustaining discharges clearly depends upon the number of charge carriers present and this in turn is a function of the rate of their formation by collision with externally supplied electrons or absorption of radiation and the rate of recombination, which destroys a fraction of the charge carriers before they can give up their charge to the electrodes. If N univalent ion pairs are produced per cc. per second and if the electrodes are r cm. apart, the saturation current density is given by

$$i_s = N \cdot r \cdot e_0 \ . \tag{12}$$

This means that the saturation current density depends only on the total number of ions produced per second between the electrodes and hence it increases with the volume of the gas enclosed, *i.e.* with the distance between the electrodes. Likewise, the applied potential at which the saturation current density is reached is similarly increased.

If the applied potential difference across the electrodes is enough for *collisional ionisation* to take place, there is of course no saturation current, the current increasing rapidly with increasing potential. This type of non self-sustaining discharge occurs in gas filled photocells, for example. The rapid increase of current with potential indicates that the original current is beginning to be amplified by means of collisional ionisation. The amplification factor is given by equation (8) and depends on the type of gas used, the pressure, and the field strength. In a homogeneous field (plain parallel electrodes) it follows from (8) and (9) that

$$\ln f = A \, p \, r \cdot e^{-B \cdot p/F} \ . \tag{18}$$

The amplification factor hence increases exponentially with the field strength. From this equation it may also be seen that at very low pressures ($p \rightarrow 0$) and for very high pressures ($p \rightarrow \infty$),

$\ln f = 0$, *i.e.* $f = 1$, so that no amplification occurs. This is because at small pressures, the mean free path of the electrons is so large that only a few collisions with the gas molecules occur, whilst at high pressures the mean free path of the electrons is so small that they have insufficient chance of gaining enough kinetic energy to cause ionisation. Hence, f passes through a maximum at a certain pressure p_0, the value of which, obtained by differentiation of (13), comes to

$$p_0 = F/B, \qquad (14)$$

i.e. it is proportional to the field, as is confirmed experimentally.

At certain values of F (again depending on the gas pressure) the non self-sustaining discharge changes in nature and becomes a self-sustaining glow discharge which hence continues independently of further supply of external energy (see next section).

Further practical examples of non self-sustaining gas discharges in addition to the vacuum photocell already mentioned are seen in the measurement of intensities of radiation by the ionisation chamber method and in the arc with independently heated cathode, but these are outisde the scope of the present section.

3. Self-Sustaining Discharge in Gases

(i) *Introduction*

If an increasing potential is applied to the electrodes in a discharge tube containing gas at a few millimetres pressure, then firstly, in the region of non self-sustaining discharge, there is obtained a current-voltage relation similar to that of Fig. 62 up to the point at which the saturation current is reached, when it appears that no further increase of current can take place (see above, p. 490). As the field strength is increased, however, the drift velocity of the charge carriers, and hence their kinetic energy, continuously increases. When it becomes large enough for the charge carriers to cause ionisation of the molecules with which they collide, and the positive ions are produced in sufficient number to release electrons at the cathode upon impact, new charge carriers are produced and these in turn produce ions by the colli-

sional mechanism so that the number of ions present increases in avalanche fashion, and correspondingly the current rapidly increases (see equation 7) [1].

The *condition for the change from a non self-sustaining to a self-sustaining process of discharge* can be seen as follows. It must first be realised that the processes taking place at the cathode and anode in gaseous discharge are entirely different. The negative charge carriers, consisting of negative ions or electrons, are discharged at the anode. The energy liberated at the anode (*i.e.* the kinetic energy of the discharging ions and the thermionic work function of the electrons) is converted almost entirely into heat, and hence charge carriers are not emitted at the anode, except in the rare case of emission from hot anodes, mentioned on p. 488. On the other hand, the cathode takes up not only the positive charge carriers but can also emit electrons provided that the positive ions striking the cathode can impart to the electrons energy in excess of the cathode work function. Stationary self-sustaining discharge obviously begins when each electron thus liberated at the cathode brings about a sufficient energy change in the gas, on its passage through it, to lead to the liberation of at least one further electron from the cathode. The mechanism of this generation of electrons is as follows. An electron, on leaving the cathode, undergoes acceleration in the electric field and imparts energy to the gas molecules in collisions. Some of the particles involved in these collisions, *i.e.* the positive ions, transport a part of this energy back to the cathode and on their impact with the latter this energy is utilised in the liberation of further electrons.

Other processes may also be contributing in this "back transport" of energy to the cathode. Thus, *e.g.*, energy in the form of light quanta emitted in the discharge, when incident on the cathode, may cause photoelectric emission.

The *quantitative condition for the onset of self-sustaining discharge* may be derived directly from equation (6) provided only the transport of energy back to the cathode by positive ions is taken into account and a homogeneous field is assumed. N_0 primary electrons produce $N_0 e^{ar}$ electrons at the anode. Of these, $N_0(e^{ar} - 1)$ have

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[1] In this, ionisation by electrons plays the most important part (see note 1 p. 485).

been formed in the gas as secondary electrons and a corresponding number of positive ions is therefore also produced. Each primary electron hence produces $e^{a\tau} - 1$ positive ions in the gas. Each of these positive ions must produce a yield of ζ new electrons at the cathode so that at least one new electron per original electron emitted is produced. Hence the condition for spontaneous discharge is

$$\zeta \left(e^{a\tau} - 1 \right) = 1 . \tag{15}$$

(ii) *Glow Discharge*

The principal forms of self-sustaining gaseous discharge are (in order of increasing current) the glow and arc discharges, of which the heavy current carbon arc is of special importance. It is only possible to understand the phenomena occurring when one takes into account the fact that even with plain parallel electrodes the electrical field in these discharges is not homogeneous, but very strongly distorted. If the potential-distance relation in a low pressure glow discharge tube is established by means of wire probes, the curve given in Fig. 77 is obtained. It can be seen that the largest part of the potential fall occurs in the neighbourhood of the cathode. This *"cathode fall"* is the most important part of the
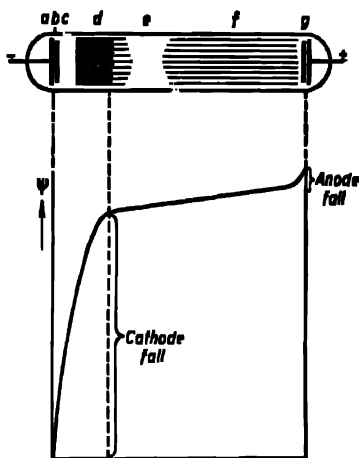
Fig. '. Potential-distance relation in a glow discharge

glow discharge. In a certain current range it depends entirely upon the gas and the material of the cathode and is independent of the gas pressure and current (normal cathode fall). Thus, with platinum electrodes in air it is about 400 volts and increases with the electronegativity of the gas and work function of the cathode material. A second, much smaller, potential fall is observed at the anode (*"anode fall"*). In the middle space between the electrodes the potential falls gradually and linearly.

The cause of the considerable distortion of the field near the cathode [1] is to be found in the formation of *"space charge"*. The passage of current occurs principally by transport of ions to the cathode and electrons to the anode. In passing through the same potential difference $\Delta\psi$ both the (univalent) positive ions and the electrons obtain a kinetic energy given by

$$e_0 \cdot \Delta\psi = \frac{m\,v^2}{2}\,. \tag{16}$$

Since the electrons are of a smaller mass than the positive ions by a factor of $1888A$ (A = atomic or molecular weight of the positive ions) they attain a velocity $\sqrt{1888\,A}$ times greater than that of the positive ions. Furthermore, the mean free path of the electrons is much larger than that of the ions, owing to their smaller size, and this again leads to an increase in speed because they can pass through a larger potential difference $\Delta\psi$ before they lose energy at the next collision. Simple kinetic theory shows that the velocities of the electrons and positive ions are in the ratio

$$\frac{v_-}{v_+} = 102\,\sqrt{A}\,. \tag{17}$$

This large difference between the speeds of the positive ions and electrons gives rise to the space charge, and the potential distribution relation of Fig. 77, in the following way. Neglecting the primary electrons emitted from the cathode, then in the middle section of the discharge tube [2] the number of electrons and positive ions must be the same because in each ionisation process both a positive and a negative ion is produced. This region is therefore free from space charge. Let the number of particles/cc. again be N. Then, in the middle of the discharge tube,

$$N_+ = N_-\,. \tag{18}$$

The current density is thus given by

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[1] The field strength is given from (I, 79) by the tangents to the curve of Fig. 77, *i.e.* it is given by $-\partial\psi/\partial x$.

[2] That is the region in which the fall in potential is linear with distance. In this region $\dfrac{\partial\psi}{\partial x}$ is constant, *i.e.* $\dfrac{\partial^2\psi}{\partial x^2} = 0$. According to equation (I, 20) this means that the space charge density ϱ vanishes and hence that the number of positive and negative ions is the same. This region is called the "positive column".

$$i = i_+ + i_- = e_0 N_+ \cdot v_+ + e_0 N_- \cdot v_- \ . \tag{19}$$

From equations (17 - 19) it follows that

$$\frac{i_-}{i_+} = \frac{v_-}{v_+} = 102 \cdot \sqrt{A} \ . \tag{20}$$

According to (20), therefore, in a space charge free region of the discharge the electrons carry at least 100 times as much current as the positive ions.

In the neighbourhood of the cathode, the current will be effectively carried only by the positive ions, and near the anode only by electrons, again neglecting the primary electrons from the cathode. Now i_+ at the cathode must equal i_- at the anode, and therefore,

$$\frac{e_0 N_- \cdot v_-}{e_0 N_+ \cdot v_+} = 1, \quad \text{or} \quad \frac{e_0 N_-}{e_0 N_+} = \frac{\varrho_-}{\varrho_+} = \frac{v_+}{v_-} \ , \tag{21}$$

if the space charge density is termed ϱ. It follows from (21), therefore, that at the cathode there is a large positive space charge whilst at the anode there is a small negative space charge, the ratio of $\varrho_+ : \varrho_-$ being at least $102\sqrt{A} : 1$, as follows from (20) [1].

A characteristic of glow discharge is the phenomena which arise by excitation of the atoms and molecules and which are schematically represented in Fig. 77. The interior of the tube consists of a series of luminous layers and of dark spaces and these are most clearly distinguishable in the case of the pure rare gases.

(a) The *Aston dark space* lies just at the cathode and is generally very thin so that it is often not observed. It occurs because the primary electrons produced from the cathode have as yet insufficient kinetic energy to bring about excitation of the gas.

(b) In the *cathode glow* region the primary electrons excite the gas by collision so that it becomes luminous, the spectral lines successively appearing in the order of increasing excitation energies from the negative boundary of the cathode glow towards the anode.

(c) In the *Crookes dark space* the primary electrons already have such a high speed on account of the rapid acceleration which takes place in the cathode fall, that the probability of excitation begins to decrease again [2]. Hence the intensity of

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[1] It follows from the POISSON's equation (I, 20) that at very positive values of ϱ the potential curve must be strongly concave downwards. If ϱ be small and negative, the curve is slightly concave, upwards.

[2] The intensity of a spectral line as a function of the energy of the incident electron (Excitation function) passes through a maximum and then at higher electronic velocities decreases again.

the light is less and the space appears relatively darker than other regions.
(d) This *cathode boundary of the negative glow* has a fairly sharp boundary on the
cathodic side, while its brightness falls off gradually on the anodic side. In this
region the primary electrons are in the presence of not only neutral particles, but
also a considerable number of ions and electrons (the *"plasma"*) [1]. The field of
the latter causes considerable retardation of the electrons, so that their velocity
again approaches that of the optimum of the "gas excitation function". The spectral
lines now appear in decreasing order of their excitation energy.
(e) On arrival inside the *Faraday dark space*, the electrons have largely lost their
kinetic energy and are no longer able to excite the gas molecules.
(f) The *positive column* is usually by far the brightest and largest section of the whole
discharge tube. This is the region of the small potential gradient where the current
is carried almost entirely by electrons. The column may appear uniform and with-
out a specific structure, or strictly in the form of laminae divided by alternate
dark spaces. In monatomic gases, the differences in energy across the dark space
between two striations is equal to the lowest excitation energy of the gas, from which
fact it is clear that the electrons at times lose their energy by carrying out excitation
in one layer and start again from zero energy in the next. In molecular gases the
relations are considerably more complicated because of the energy transfer to the
rotational and vibrational degrees of freedom of the molecules, as is clear from
the fact that for molecular gases the occurrence of striations depends upon gas
pressure and current strength.
(g) In the anode fall the electrons again reach sufficiently high velocity to be able
to cause ionisation shortly before reaching that electrode; this gives rise to the
anode glow.

(iii) *The Arc*

If the current density in the glow discharge exceeds a certain
value the cathode fall becomes greater and increases with current
density ("*anomalous glow discharge*"). With further increase of
current density the cathode fall passes through a maximum and
then very rapidly decreases to about $1/10$ of its former value while
the current density increases very slowly. This form of discharge,
characterised by small cathode falls and large current densities at
the cathode, is termed the arc. It is produced by the fact that,
owing to the high c.d., the cathode becomes so hot that it fuctions
as a "*hot cathode*" and is thus effectively a very intense source of
electrons. Here also, as in glow discharges, the cathode plays the
main role in the discharge. The dependence of the arc on the high

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[1] The plasma is the general name given to the mixture of neutral particles, ions
and electrons in the discharge.

temperature of the *cathode* can be deduced from the fact that it only operates between an electrolytic solution and a carbon electrode when the solution is the *anode*. Measurements of cathode temperatures show that the discharge current is approximately equal to the thermionic emission current, as calculated from RICHARDSON's equation (12), thus confirming the thermionic theory of the arc. The lowering of the cathode fall compared with that of glow discharge depends on the fact that the electrons sent out from the hot cathode neutralise the positive space charge in its neighbourhood; this can also be brought about artificially in a glow discharge by using an independently heated cathode.

The thermionic theory of the arc is only valid when the cathode consists of non-volatile substances, *e.g.* carbon or tungsten, and is quite inapplicable for other more volatile, *e.g.* liquid metal, cathodes. The best example of the latter type is the arc in a mercury vapour lamp, where a small luminous spot can be seen to be moving erratically over the mercury surface. The cathodic current density is high, owing to the small area of the hot spot and probably amounts to several thousand amps per sq.cm. The temperature of the spot can be calculated from the rate of evaporation of the mercury and is only about 300 °C. This shows at once that the mechanism of the arc in mercury cannot depend on thermionic emission of electrons. To explain the high current densities, it is assumed that at a small distance from the liquid cathode there is a layer of vapour at a very high temperature, *i.e.* about 4,000°; and in this region, considerable thermal ionisation would be expected to occur [see equation (10)]. The current between the cathode and the above mentioned layer is regarded as carried exclusively by positive ions, there being then no need for electron emission from the cathode, in spite of the high current density. The energy gained by the positive ions on their passage through the cathode fall is partly transferred to the gas and thus serves to compensate for heat losses in the vapour layer.

According to equations (10) and (11), both electron emission at a hot cathode and thermal ionisation of a gas increase exponentially with temperature, so that a considerable increase of the number of ions and electrons with temperature must occur. Their mobilities also increase in the same sense so that the resist-

ance of the arc decreases rapidly with increasing temperature and hence with increasing current strength. The ratio, E/i, the resistance, (see p. 9), is hence not constant either in a glow discharge or in the arc; the potential difference drops with increasing current so that OHM's law is disobeyed. This type of the potential-current relation is said to have a *"falling characteristic"*. The relation between E and i can be represented by the equation

$$E = a + b/i, \tag{22}$$

from which it can be seen that if the distance between the electrodes is fixed, there is a hyperbolic fall of potential difference with increasing i (see Fig. 78).

It follows from the above that a conductor with falling characteristics should never be connected to a constant source of potential unless it is in series with an ohmic resistance, because a slight increase in current causes the arc resistance to decrease whereupon the current would increase indefinitely and the system burn itself out. Inclusion of an ohmic resistance causes the total resistance of the system to increase again with increasing current after passing through a minimum, as can be seen from Fig. 78. As the strength of the current increases the potential difference across the ohmic resistance increases and therefore that across the arc drops so that the applied potential difference must be increased to maintain current in the arc, *i.e.* at a given applied potential difference, the current through the arc falls back to the equilibrium value. Con-

Fig. 78. Current-voltage curve for the luminous arc (falling characteristic)

versely, if the current in the arc falls, then the potential difference applied to the arc increases owing to the increased resistance of the arc, so that the original current in it is restored. In the absence of the resistance, the arc would simply go out in this latter case.

It has already been seen (see p. 225) that in ionic conduction the conductance increases with increasing temperature so that as the applied potential is increased, the resistance must fall, *i.e.*, the current-voltage relation exhibits a falling characteristic. A practical example of an ionic conductor possessing these characteristics is glass. If a potential of a few hundred volts is applied to a section of glass and the latter is warmed to red heat with a BUNSEN burner, a current begins to flow which increases without any additional warming until the glass has melted, because the current flowing when the bunsen is removed causes further heating,

and hence reduction in resistance, whereupon the current strength through the glass is increased and so on. On this account, the "NERNST filament" [1] must always be used with an external resistance in series.

In gases at relatively high (*e.g.* atmospheric) pressure no self-sustaining glow discharge would be expected ($f = 1$). At sufficiently high cathode temperatures, an arc discharge may however occur. To strike an arc in such a case the electrodes have therefore to be brought momentarily together; as they are removed from contact the resistance between them becomes very large so that the cathode heats up enough to commence thermionic emission. At very high applied potential differences a self-sustaining discharge can commence between cold electrodes, this being again caused by collisional ionisation in the neighbourhood of the electrodes, where stray electrons cause an avalanche effect to take place (see p. 486). With increasing applied potential, therefore, a thin layer of light is observed at the electrodes; this occurs particularly in a markedly inhomogeneous field and may spread to the space around the electrodes ("Corona", "Brush" and "point discharge"). Since collisional ionisation increases with increasing voltage, a sufficient increase of potential may lead to a complete breakdown of the gap between the electrodes. This is called a spark discharge. The condition for discharge across the gap to occur is given by equation (15), *i.e.* discharge commences when every electron formed at the cathode brings about a sufficient number of ionisations on its way to the anode so that at least one new electron is set free at the cathode by means of positive ion bombardment. If a condenser of high capacity is introduced into the circuit, the current strength of the resultant discharge may become very large ("condensed discharge"). This is often made use of to increase chemical decompositions in discharges (see Section 4).

In *alternating current arcs* the processes are more complicated because the arc is momentarily extinguished every time the current changes direction. At the commencement of each half

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[1] The NERNST filament consists of a mixture of ZrO_2 with rare earths (Y_2O_3 and Er_2O_3). It is initially heated to about 600° by an auxiliary wire heater, after which a cut out stops current flow through the wire heater and passes it through the now highly conducting NERNST filament.

cycle the applied potential begins to rise, but no arc can be immediately formed because the gas and electrodes have cooled considerably whilst the current was low. At first there is a glow discharge with rising characteristic in which the conductance of the gas and the temperatures of the electrodes increase by col-lisional ionisation. For the arc discharge to commence, the applied potential must reach the striking voltage A (see Fig. 79). When this is reached the nature of the discharge is changed and a falling charac-teristic AB is observed until the current reaches its maxi-mum value after which the cur-rent starts to decrease, because of the decreasing potential of the A.C. source. The cooling produced during this time leads to an increase of potential between the electrodes but this does not reach the previous magnitude, *i.e.* the striking voltage. At the voltage C the

Fig. 79. Characteristics of the alternating current arc

arc is extinguished (C is called the extinction voltage), glow discharge begins again, the potential (following the phase of the A.C.) passes through 0 and the series of changes recom-mences in the second half cycle.

The current-voltage characteristics in the A.C. arc discharge exhibit hysteresis. Only the section AB, BC and the corresponding parts for the other half cycle, actually belong to the arc process. With increasing frequency the cooling during the period of inter-ruption of the arc becomes less and less so that the striking voltage is reached earlier and points A and C move closer together. If the frequency is finally so high that temperature and con-ductance during a half cycle hardly change, the current and po-tential become almost proportional to one another, and the characteristic becomes a straight line passing through the origin.

For chemical reactions taking place in a discharge, the frequency of the A.C. used is often very important (see p. 508). High frequency discharges often increase the yield in chemical reactions very considerably. It is simple to produce high frequency oscillations by excitation with a spark (see Fig. 80). The spark gap *F* is connected to the secondary coil of a transformer *T* functioning from an ordinary 50 cycle source and serves to connect it with an oscillatory circuit consisting of a capacity *C* and self inductance *L*. If the voltage in the spark gap reaches the striking value the spark thus produced closes the oscillatory circuit, which, upon receipt of the pulse thus imparted to it, commences to oscillate with its characteristic frequency. The energy of the oscillations is transferred by inductive coupling to a secondary circuit in which the discharge tube is connected. By use of an auxiliary circuit, it can be arranged that the primary circuit *P* becomes interrupted after delivery of energy to the secondary circuit *S*. [1] In this case, the excitation in the secondary circuit is of an impulsive type.
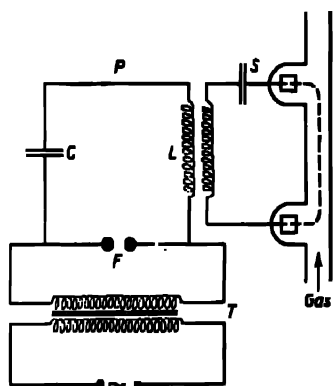
Fig. 80. Induction of gas reactions by means of high frequency discharges (schematic)

High frequency discharges can also be produced in a gas contained in a glass tube using external electrodes, *e.g.* a coil connected to the secondary circuit may simply be wound round the discharge tube; this method eliminates effects of the metal electrodes on the products of the reaction (*e.g.*, atomic recombination reactions, which are strongly catalysed by metals).

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[1] For the interruption of the primary current a very short spark gap is used between metal plates of a material of high thermal conductance. In consequence of the beats between the e.m.f.'s in the two circuits, the spark goes out when the minimum beat intensity is reached. On account of the rapid cooling of the electrodes and the gas between them the spark gap does not suffer a renewed breakdown by induction from the secondary, so that the energy is almost completely transferred to the secondary circuit.

(iv) *The Heavy Current Carbon Arc*

One of the reasons why electric discharges are of particular significance to chemistry is that they provide the most effective method for the *production of very high temperatures*. In chemical reactions, temperatures higher than 2000 - 3000° are seldom obtained because of the dissociation of the products of combustion (the temperature of the hydrogen-oxygen flame is about 2000°; and the thermite reaction between Al and metal oxides of the order of 3000 °C.). In very rapid reactions (explosions) it is possible to reach much higher temperatures but these can only be maintained for a fraction of a second. Neither mechanical (*e.g.*, adiabatic compression), nor concentrated irradiation methods give rise to very high temperatures. One method of obtaining very high temperatures involves the spark discharge in which process large amounts of energy are liberated in a short time; but the duration of the phenomenon is very short (10^{-3} - 10^{-7} sec., according to the conditions for discharge). In practice, the most important method for the attainment and maintenance of high temperatures is the electric arc. The temperature of the core of the usual carbon arc in air at atmospheric pressures has been estimated by various methods [1] (*e.g.*, by the intensity distribution of the rotational lines of the CN bands) to be about 7000 - 8000 °C., and varies somewhat according to the loading on the arc. The arc therefore plays an important role in technical electrochemistry for carrying out reactions at high temperatures (*e.g.* production of calcium carbide, calcium cyanamide, silicon carbide, ferrous alloys, artifical graphite, steel, acetylene, and so on).

In recent years it has been possible to obtain higher temperatures than those mentioned above by very heavy loading of the usual carbon arc. It has been shown [2] that in these high current arcs a new type of discharge occurs which is essentially different from that of the usual arc. It commences at currents greater than 40 amps and particularly when anodic current densities up to 800 amps/cm.^{2} (obtained by using correspondingly thinner poles) are used. This type of discharge possesses markedly different

[1] See R. MANNKOPF, *Z. Physik*, 1934, **120**, 228.

[2] See W. FINKELNBURG, *Z. Physik*, 1942, **119**, 206; *Chem. Fabrik*, 1942, **15**, 141.

characteristics from those of the ordinary arc. They are illustrated in Fig. 81 for various forms of high current arc, possessing anodes of ordinary carbon, or of carbon provided with a potassium silicate or cerium fluoride core. It can be seen from the figure that there is an initial fall of potential with increasing current as in the usual carbon arc, but that at higher current strengths the potential passes through a minimum and then a rising characteristic again appears. The slope of this, as well as the position of the minimum, depend on the material of the anode but are entirely independent of the cathode material.
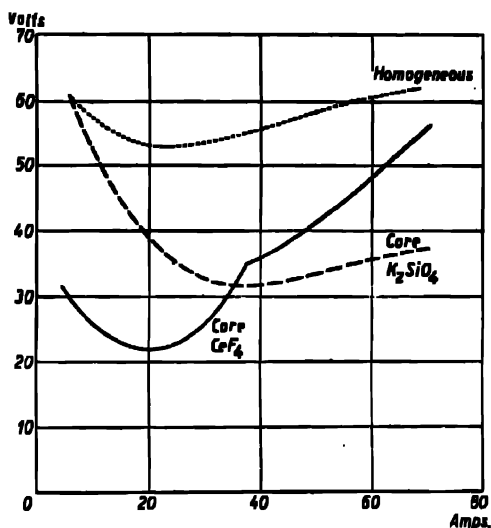
Fig. 81.

Characteristics of the high current carbon arc

The heavy loading of the anode causes considerable evaporation of the anode material and this leads to the emission of an intense beam of vapour in a direction perpendicular to the top face of the anode. This is the origin of the "anode flame". The evaporation of the anode necessitates an increased energy supply which is derived from the anode fall, which grows with increasing current strength. Due to these competing processes a minimum appears on the current-voltage diagrams. It has been shown by means of probe measurements that the rising characteristic on this diagram is due to a cathode fall and independent of the current strength and also in the positive column an anomalous anode fall which increases with current strength.

The vapour of the anode flame is heated in the anode fall to more than 8000° and consists of a strongly ionised plasma (see p. 496) which generally cools (mainly by radiation) as it leaves the anode. Probe measurements show that inside the anode flame

there is no potential difference, so that this flame itself does not take part in the conduction process and is therefore particularly suitable for a study of the state of a plasma produced thermally. Since the anode carbon can be cored with any solid substance and since this vapourises simultaneously with the carbon, reactions at very high temperatures can be studied, usually by spectroscopic methods. The high temperature of the anode vapour makes the heavy current carbon arc the most intense source of light known (intensity of illumination more than 10^5 lumen).

At high current densities (100 - 160 amps) a new phenomenon known as the "negative pilot flame" appears which is independent of the material in the carbon and the processes at the anode. The whole length of the arc from the hot spot on the cathode becomes markedly constricted and the current densities rise up to about 8000 amp/cm.[2]. This contraction of the arc can be attributed to the effect of the magnetic field due to the discharge itself. Spectroscopic examination of the radiation emitted from the constricted arc shows that in the interior of the columns there are atomic lines superimposed on a continuum, but molecular bands are absent, thus indicating that very high temperatures exist inside the constricted part of the discharge. In the interior of the column these are estimated at 15,000 °C.

B i b l i o g r a p h y : J. J. and G. P. THOMPSON, *Conduction of Electricity through Gases*, I and II, Cambridge, 1928; L. B. LOEB, *Fundamental Processes in Electrical Discharge in Gases*, New York, 1989; F. A. MANFIELD and R. R. BENEDICT, *Theory of Gaseous Conduction and Electronics*, New York 1941; W. FINKELNBURG, *The High Current Carbon Arc*, Berlin, 1948.

4. Chemical Reactions taking place under the Influence of the Electric Discharge

(i) *Introduction*

Although the observations of CAVENDISH and PRIESTLEY on the combination of nitrogen and oxygen to nitric oxide in an electric discharge in air belong to one of the first discoveries of electrochemistry (see p. 1), the study of the electrochemistry of gases

is still in its early stages. Most electrochemical gas reactions of commercial importance are more accurately termed *electro-thermal*, *i.e.* the arc is used simply to attain a satisfactory position of equilibrium, as in the production of endothermic substances such as calcium cyanamide, calcium carbide, and nitrous oxide (BIRKELAND and EYDE process, now obsolescent).

Special chemical processes have been observed in reactions occurring in discharge tubes which depend upon specific effects caused by the arc itself and can be regarded as *true electrochemical gas reactions*. The field of these reactions is as yet insufficiently developed to make a comprehensive theoretical treatment possible, as is clear from the fact that no satisfactory account of the plasmatic state of a gas can as yet be given. The subject must therefore be discussed with reference to a few special cases about which some approximate qualitative theories are already available.

(ii) *The Dissociation of Diatomic Molecules*

In the glow discharge in hydrogen at low pressure (0·1 to 1 mm.) the band spectrum of hydrogen can be observed in the neighbourhood of the electrodes. At some distance from the electrodes, the BALMER spectrum of the hydrogen atom can be detected. This fact alone does not necessarily prove that free hydrogen atoms are present in notable concentrations in the discharge tube, because emission of the BALMER lines could be caused by the momentary formation of normal and activated hydrogen atoms by collision between activated molecules. The presence of appreciable quantities of atomic hydrogen in the tube can, however, be directly proved by removing some of the streaming gas from the middle of the tube, and causing it to react with various substances outside the discharge tube. It is found that this gas causes reduction of numerous metallic oxides, sulphides, halides, *etc.*, to the metal and that metalloids such as sulphur, arsenic and phosphorus are reduced to the corresponding hydrides. The concentration of atomic hydrogen can be estimated approximately from a quantitative examination of the chemical reactions which it causes. It is found to depend upon the current strength as well as upon the other factors influencing the discharge (*e.g.* pressure, frequency, etc.)

and may correspond to almost the complete decomposition into atoms of the hydrogen molecules present.

If metal wires are introduced into the path of the discharge, strong thermal effects are observed (*e.g.*, the wires begin to glow) and in their neighbourhood the intensity of the atomic spectrum becomes much less than that of the band spectrum. It can be shown from conductance measurements that these thermal effects are not due to ionic recombination processes so that they must be ascribed to the recombination of hydrogen atoms to molecules under the catalytic influence of the metal. This is the reason for the absence of the atomic spectra in the neighbourhood of the electrodes. [1] The relative effectiveness of the metal wires as catalysts runs parallel to their hydrogen overpotential (see p. 431). These experiments carried out at a given current density on various electrode materials prove conclusively that the "active hydrogen" of the discharge tube is in fact atomic hydrogen, probably formed largely by the collision of electrons with the hydrogen molecules.

Information concerning the *mechanism of the collision process* can be obtained from the dependence of the intensity of the BALMER spectra on the current. Two possible mechanisms must be considered: firstly, the formation of hydrogen atoms and their excitation to emission may take place by means of two different electron impacts. In this case, the intensity of the emission would be expected to depend on the square of the current, because the two processes take place independently of one another and each should be roughly proportional to the current. Secondly, the primary process may consist of an initial decomposition of the molecule into an excited and unexcited atom, so that the emission of light occurs on the first electron impact and therefore the intensity of the emission should be roughly proportional to the current. Experiment shows that the emission intensity depends

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[1] The atoms can only combine at solid surfaces or in three body collisions because otherwise the dissociation energy liberated (about 100 kilocals) causes the molecules to dissociate again. Apart from metals, various other substances such as the glass walls of the discharge tube catalyse the atomic combination. Small traces of oxygen "poison" the catalysis on the walls of the tube (presumably by absorption of water) and thus increase the yield of active hydrogen.

upon the square of the current, so that the first mechanism is the correct one.

As the above mentioned *reducing action of atomic hydrogen* shows, this substance is highly reactive, even at room temperatures. Thus, for example, various hydrides which cannot be formed with ordinary hydrogen such as those of silver, lead, beryllium, gallium, indium and mercury, can be produced [1] with atomic hydrogen. Reactions with hydrocarbons, involving emission of C_2^- and CH^- bands, give rise simultaneously to hydrogenation, dehydrogenation and chain splitting [2].

A disadvantage of the glow discharge tube method of producing atomic hydrogen is that only small pressures can be used, because at pressures greater than a few mm. of mercury, the glow discharge ceases. The atomic hydrogen cannot therefore be led directly to *solutions or liquids* because at ordinary temperatures the liquids would possess vapour pressures (*e.g.* water at 0 °C., 4·58 mm.) such that the vapour would transfer itself to the discharge tube. If, however, helium or neon at about 20 mm. pressure is added to hydrogen at a pressure of a few tenths of a mm., the glow discharge is practically unaffected and the gas leaving the discharge tube passes through liquids in which its reactions can be studied [3].

Atomic hydrogen is also formed in high concentration in the *luminous arc*. The latter can only be maintained in hydrogen at atmospheric pressures by the use of high applied potentials (several hundred volts) because the long half life period of atomic hydrogen does not allow the continuous energy loss necessary for a stationary state to occur by radiation or conduction but only by diffusion processes. The large heat of dissociation which is liberated during the recombination of the atoms can also be used for the production of high temperatures in a hydrogen stream which is blown between the two tungsten electrodes of an arc thus enabling difficultly weldable special steels to be joined in the complete absence of oxygen.

[1] See E. Pietsch, *Z. Elektrochem.*, 1933, **39**, 577.
[2] In the production of acetylene from saturated hydrocarbons (*e.g.* methane) in the direct current arc (a process which has recently gained technical importance) Balmer lines as well as C_2^- bands are observed.
[3] See P. Harteck, *Z. Elektrochem.*, 1936, **42**, 536.

Atomic oxygen is also produced in the glow discharge tube in an analogous way. The atomic concentration can be estimated by measurements on the heat of dissociation which show that it may be as high as 20%. The intensity of the spectral lines of atomic oxygen is proportional to the square of the current so that dissociation and excitation are separate processes. The atoms have a comparatively long life and reactions with atomic oxygen can hence be examined outside the discharge zone. It is found to react with most organic substances at room temperature, OH, CH and CC band spectra as known from the corresponding ordinary combustion process being observed. Reactions with molecular hydrogen and carbon dioxide are remarkably slow. Various addition reactions are observed at low temperatures. For the examination of reactions with liquids, rare gases are added to the atomic oxygen as in the technique described above for atomic hydrogen.

Atomic oxygen is also regarded *as an intermediate* in the production of *ozone* in the "silent discharge" [1]. Ozone is a highly endothermal compound (heat of formation $+ 34.5$ kilocals) and it cannot be satisfactorily prepared by a thermal reaction even at the high temperature of the arc. It is found, however, that a considerable yield of ozone is obtained when air or oxygen at atmospheric pressure are subjected to the silent discharge, a dielectric (glass) acting as the adjustable resistance in the discharge tube circuit. A stationary state is set up, some part of the ozone decomposing again at higher concentrations. Various experiments on the mechanism of ozone formation have shown that it involves oxygen atoms. The reaction $O + O_2 \rightarrow O_3$ has only a small activation energy, about 4 kilocals., and occurs by means of three body collisions or on solid surfaces, as in the recombination of oxygen atoms to molecules. The effectiveness of different third bodies varies considerably according to the atoms involved; thus for oxygen it is four times greater than for nitrogen and eight times as great as that for argon. The yield of ozone can be largely increased by means of high frequency alternating current and under good conditions yields of 250 g. ozone per kilowatt

[1] This is the discharge of a high voltage through a glass wall (SIEMENS Ozonizor) in which no visible radiation occurs (also called "dark discharge").

hour are obtained, corresponding to an efficiency of 20% of the electrical energy input.

Nitrogen is activated on electric discharge. This is manifested by the appearance of a yellow glow which is dependant upon the intensity of the condition of the discharge. This glow may persist for several hours.

The band spectra of nitrogen in the discharge consist of several "positive and negative groups", depending upon whether these are observed in the positive column or the cathode fall of the discharge. The positive bands correspond to conditions of a smaller excitation energy and are caused by emission from neutral excited molecules, whereas the negative bands of higher energy are emitted from N_2^+ ions. In the negative glow there are also lines due to nitrogen atoms and N^+ ions, these entities being essential prerequisites for the existence of the *"active"* *nitrogen* which is responsible for the glow.

Electron bombardment experiments on nitrogen have shown that direct dissociation of the molecules into atoms (dissociation energy, 7·34 e.volts) does not occur, as it does with hydrogen and oxygen, but that the decomposition takes place by way of higher energy levels in the molecule, and particularly through the first excitation level of the N_2^+ ions. This explains why the atomic spectrum is only seen in the negative glow where at the given value of the mean free path the electrons gain a much higher energy due to the cathode fall. If it is desired to produce *very highly active nitrogen*, a "condensed" discharge is used, a large capacity being included in the discharge circuit. It is found that the higher the capacity and hence the greater the current upon discharge, the more the spectrum is shifted towards the N_2^+ bands and the nitrogen lines and the greater is the concentration of nitrogen atoms and the strength of the afterglow. *Nitrogen atoms are hence responsible for the activity and afterglow of nitrogen.*

Various spectroscopic examinations indicate that the *mechanism of the afterglow in nitrogen* is as follows. The chemiluminescence of active nitrogen takes its energy from the recombination energy of atomic nitrogen, the excitation, however, not occurring directly but via a series of intermediate products. In the combination of

two unexcited nitrogen atoms, which is only possible at solid surfaces or in three body collisions, metastable molecules are formed with an energy of 6·14 e.volts, thus,

$$N + N + N_2 \rightarrow N_2 + N_2^m . \tag{23}$$

These metastable molecules have a long life period of about 10^{-1} sec. On collision between them metastable atoms are formed, e.g.,

$$2N_2^m \rightarrow N_2 + 2N^* . \tag{24}$$

The energy of these metastable atoms is found to be 2·37 and 8·56 e.volts respectively, according to conditions in the discharge tube. They can then surrender their energy in a further collision with mestatable molecules and raise the energy of the latter to a higher energy state, i.e.,

$$N^* + N_2^m \rightarrow N_2^* + N . \tag{25}$$

The production of metastable molecules and atoms hence always occurs at the cost of the recombination energy of the N atoms, thus confirming that active nitrogen is essentially atomic. This is also in accord with the fact that active nitrogen from which atomic nitrogen is removed ceases to cause an afterglow, although owing to the presence of the remaining metastable molecules, it retains its power of exciting other atoms or molecules and bringing about chemical reactions ("non-luminous" active nitrogen). For example, if hydrogen is present during the discharge, atomic nitrogen is completely removed because the atomic hydrogen formed reacts with it to form ammonia (see p. 514). Hence, addition of hydrogen extinguishes the afterglow of active nitrogen almost completely yet the metastable molecules present can still for example excite mercury atoms to chemiluminescence. The fact that in the case of nitrogen the activity cannot be ascribed to the presence of ions can be demonstrated in that removal of the ions by means of a weak electric field, causes neither the afterglow nor the high reactivity to be lost.

Reactions involving atomic nitrogen are numerous and have not as yet been systematically examined. Qualitatively, it has been found that various previously undiscovered metal nitrides can be formed with atomic nitrogen. A quantitative determination

of the concentration of the latter can be carried out with an excess of nitric oxide, which reacts with atomic nitrogen in two stages to form nitrogen trioxide as follows:

$$N + 2NO \rightarrow NO_2 + N_2 ,$$

$$NO_2 + NO \rightarrow N_2O_3 . \tag{26}$$
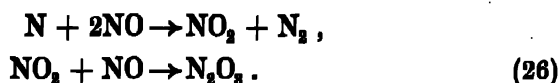
The nitrogen trioxide can be condensed and weighed.

Atomic chlorine and bromine have also been produced [1] in an electric discharge at pressures of less than 1 mm., when the line spectrum of the atoms is observed. Earlier attempts at this preparation failed because the pressures used were too high, thus bringing about rapid recombination of the atoms by three body collisions. In order to eliminate the catalytic influence of the electrodes, the gas is taken off at large distances from the electrodes, or an electrodeless ring discharge is used (see p. 502). The concentration of the atoms present in the gas can be measured by means of the heat of recombination, the heat of dissociation of the molecules being known from spectroscopic data. In chlorine, a concentration of up to 40% of chlorine atoms can be obtained in the above way. *The reactivity of atomic* chlorine is exemplified in reaction with certain other gases the photochemical chlorination of which is known to be a chain reaction. Thus, for example, a mixture of molecular hydrogen and *atomic* chlorine reacts rapidly in the *dark* to form hydrogen chloride. This fact also provides direct confirmation of the mechanism proposed by NERNST for the photochemical reaction of molecular hydrogen and chlorine.

(iii) *The Formation of Free Radicals*

If polyatomic molecules are exposed to the electric discharge, the primary dissociation process would be expected to lead to the formation of radicals and the existence of these has been established in some cases. Thus, in discharges in water vapour at low pressures a series of bands can be observed which can be attributed to the OH radical and which are *emitted* at a high intensity. The most characteristic of these bands lies at 3064 Å.

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[1] See G. M. SCHWAB and H. FRIESS, Z. *Elektrochem.*, 1933, **39**, 586; G. M. SCHWAB, Z. *Physik. Chem.*, 1934, **27B**, 452.

The same spectrum is observed *in absorption* on the thermal dissociation of water vapour above 1000 °C. Beside this characteristic band at 3064 Å, the BALMER spectrum of the hydrogen atoms, the band spectrum of the hydrogen molecule and, in lesser intensity, the line spectrum of the oxygen atom are also observable. The intense emission of the OH spectrum led initially to the concept that OH radicals might be present in large concentrations and that they possessed a long half life period similar to that of the hydrogen atoms. Actually, however, the OH radicals cannot be detected by means of absorption measurements [1] either directly after the onset of the discharge or during the discharge, from which it must be concluded that their concentration in the stationary state must be very small in spite of the intensive emission spectrum.

This apparent contradiction was explained by the examination of the dependence of the intensity of the OH bands on the current density during the discharge. Here the second of the mechanisms of activation discussed above (see p. 506) comes into play, namely that the intensity of the emission spectrum increases proportionally to the current strength, which can only be explained if the OH spectrum is emitted at the same time as the radicals are created by electron bombardment. This means that the water molecule decomposes into a normal hydrogen atom and an excited OH radical. In support of this is the fact that the intensity of the bands is independent of the material of the vessel walls; thus, if the walls contain surface impurities such as platinum, the BALMER spectrum disappears but the OH spectrum remains unaffected.

The fact that OH radicals are formed in large numbers but are hardly detectable in the stationary state (*i.e.* have no absorption spectrum) leads to the view that they are used up very quickly by some reaction. Consideration of thermal data concerning the various possible reaction mechanisms leads to the conclusion that the reaction

$$2OH \rightarrow H_2O + O \qquad (27)$$

occurs quickly and is therefore probably responsible for the disappearance of OH radicals immediately after their formation.

[1] K. F. BONHOEFFER and T. G. PEARSON, *Z. Physik. Chem.*, 1931, **14B**, 1.

It also explains the formation of the lines due to oxygen atoms which are observed in the emission spectrum and the fact that at higher current densities the dissociation of water vapour becomes more and more independent of the current strength, because the dissociation products of the discharge unite recombining to form water with increasing speed. The scheme of reactions for the decomposition of water vapour is thus thought to be as follows:

$$H_2O \rightarrow OH^* + H,$$
$$OH^* \rightarrow OH + h\nu,$$
$$H + H \rightarrow H_2,$$
$$OH + OH \rightarrow H_2O + O,$$
$$O + O \rightarrow O_2,$$

(28)
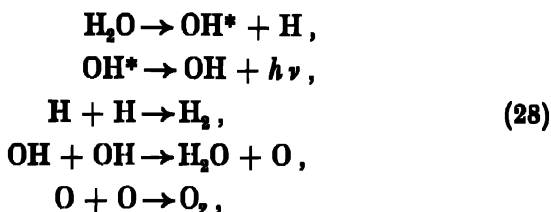
the atomic combinations again taking place either by means of three body collisions or on solid surfaces. Hydrogen peroxide is also formed to a small extent by the combination of OH radicals. As this reaction must, however, also take place in a three body collision, its velocity is much too small to account for the rapid disappearance of the OH radicals.

The contention that in homogeneous gas reactions OH radicals react mainly with each other according to (27) is also supported by the analogy of the reaction of the OH radicals produced in electrolysis. These also react to form water and atomic oxygen, the latter combining to give molecular oxygen by a second order mechanism. Attempts to prepare hydrogen peroxide directly by the anodic deposition of hydroxyl ions have likewise failed, the current efficiency being very small (cf. the small velocity of formation of hydrogen peroxide by means of OH combination in the gaseous phase).

The *free imine radical*, NH, can be detected by its characteristic emission spectrum in a glow discharge in ammonia at low pressures. Its half life period is, however, again so short that it is not possible to detect it outside the discharge tube. The spectra of hydrogen and nitrogen also occur in the discharge spectrum and the ammonia is found to be largely decomposed (up to 80%). The intensity of the NH bands decreases with increasing distance from the point of entry of the ammonia, while the intensities of the

molecular hydrogen and nitrogen bands increase so that it may be concluded that the primarily appearing NH is immediately destroyed again either by the discharge itself or by secondary reactions[1].

(iv) *Syntheses and Degradations*

The high reactivity of free atoms or radicals which occur in the discharge tube gives rise to a number of reactions which take place either in the tube itself, or, subsequently with dissociation products of the non-transient kind. These reactions are either among the dissociation products themselves or between these and added substances. Discharge in gaseous mixtures hence always leads to reactions which can be of varied character according to the nature of the primary dissociation products. Knowledge concerning the various single stages in the reactions, the distribution of excited and ionised decomposition products, the energetics of the net reaction, the activation energies of the various single stages, the effect of the discharge conditions, *etc.*, is as yet very limited. This is partly due to the fact that the experimental conditions are not easily reproducible, these causing considerable changes in the rate and even the direction of the reaction, owing to the sensitivity of the intermediate products to catalytically active impurities. A few of the less incompletely examined reactions will now be mentioned.

The reaction between *active hydrogen and active nitrogen* can be examined outside the discharge tube because of the comparatively long life of hydrogen and nitrogen atoms[2]. The two gases are activated in separate discharge tubes and introduced into a common mixing tube. The reaction products are collected in a cold trap, and quantitatively analysed. In the same way it is possible to examine the reaction of active nitrogen with ordinary hydrogen, and vice versa, simply by interrupting the discharge in one tube. Such experiments show that N does not react with molecular hydrogen, nor does atomic hydrogen react with

[1] J. K. DIXON and W. STEINER, *Z. physik. Chem.*, 1932, 17B, 327.

[2] W. STEINER, *Z. Elektrochem.*, 1930, 36, 807; J. K. DIXON and W. STEINER, *Z. physik. Chem.*, 1931, 14B, 397; 1932, 17, 327; E. TIEDE and F. HEY, *Ber. Deut. chem. Ges.*, 1933, 66, 91.

molecular nitrogen, as is in agreement with the thermodynamic data. In the reaction between active hydrogen and active nitrogen, the main product is ammonia and small traces of hydrazine are also produced, giving rise to the NH spectrum. Discharge in a mixture of the two gases considerably increases the yield of ammonia.

These observations lead directly to the conclusion that the formation of ammonia depends on a primary reaction between H and N, three body collisions being necessary to dissipate the energy in the homogeneous phase reactions

$$N + H \rightarrow NH ,$$
$$NH_2 + H \rightarrow NH_3 . \tag{29}$$
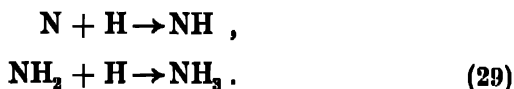
If metal catalysts are introduced into the discharge tube, the afterglow of pure active nitrogen is reduced owing to combination on the metal surface. The same phenomenon can be observed in a mixture of active nitrogen and molecular hydrogen. If atomic hydrogen is also present, however, the afterglow is completely eliminated. From these experiments it can be calculated that the reaction between H and N takes place on metal surfaces with 50 times higher velocity than in the gas phase. As the afterglow of nitrogen is dependent upon the presence of atomic nitrogen (see p. 510), this experiment also shows that the hydrogen atoms do not react with metastable nitrogen molecules. The primary process probably occurs by initial adsorption of hydrogen atoms on the metal, followed by combination to H_2, or with nitrogen atoms from the gas phase to NH. An atomic hydrogen combination must also take place apart from the NH formation as is proved by the fact that the yield of ammonia does not increase proportionally to the hydrogen atom concentration, as given by (29), but lags somewhat behind this. Whether the reaction mechanism (29) is the sole one involved in the formation of ammonia from H and N under the conditions of a discharge tube is not known. Electron impact experiments show that positive ions such as N_2^+ and N^+ are also important in the ammonia synthesis and the detailed mechanism of this reaction needs further investigation.

The earliest known electrochemical gas reaction, the *formation*

of nitric oxide by electric discharge in air, or in nitrogen-oxygen mixtures, is also not completely understood. It appears that only nitric oxide NO is formed primarily, and that NO_2 is then formed secondarily, to become oxidised to N_2O_5 and NO_3 in the presence of the ozone, which is produced simultaneously. The silent electric discharge in air produces mainly ozone (see p. 508) and also small amounts of nitric oxide; in the brush discharge, ozone and nitric oxide are both produced and react to form N_2O_5; in the arc and spark discharges, only nitric-oxide is obtained because O_3 is almost completely dissociated at these high temperatures; in the glow discharge the formation of nitric oxide is also the predominant reaction.

It has already been mentioned that the formation of nitric oxide according to the equation

$$NO_2 + O_2 \rightarrow 2NO + 43\cdot2 \text{ kcals} \qquad (30)$$
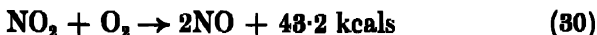
is mainly a thermal reaction in the arc. As it is strongly endothermic, the yield of nitric oxide increases with increasing temperature so that at the higher temperatures reached in the arc, the equilibrium is displaced towards the formation of nitric oxide. The following equilibria have, however, also to be taken into account:

$$N_2 \rightarrow 2N + 169 \text{ kcals} \qquad (31)$$

$$O_2 \rightarrow 2O + 117 \text{ kcals} \qquad (32)$$

$$NO \rightarrow N + O + 121 \text{ kcals}, \qquad (33)$$

i.e. the increasing thermal dissociation of molecular nitrogen and oxygen at the temperature of the arc makes the formation of nitric oxide from its atoms an appreciable reaction. This is a strongly exothermic reaction so that the equilibrium concentration of nitric oxide formed from its atoms decreases as the temperature increases. The net result of the endothermic molecular reaction (30) and the strongly exothermic atomic reaction between nitrogen and oxygen is that the equilibrium concentration of nitric oxide passes through a maximum with increasing temperature. In the stationary state a maximum yield of nitric oxide occurs and for equimolar initial concentrations of molecular nitrogen and oxygen this corresponds to $5\cdot9\%$ of NO at 3,500 °K.

It can be seen from these considerations that it is difficult in discharge tube reactions to separate purely electrical processes from purely thermal ones; thus the dissociation of nitrogen and oxygen molecules occurs by both thermal and electronic activations and it is thus doubtful if a thermodynamic equilibrium solely dependent on temperature is ever set up in the luminous arc. In the latter the temperature is not well defined because the distribution of the electron velocities in the electric field is not in accordance with the MAXWELL distribution law so that the concentration of an endothermic compound in the luminous arc may be much greater than the equilibrium value which would obtain if a MAXWELLian distribution of velocities existed. The fact that the nitric oxide synthesis in the luminous arc partly depends on direct electrochemical effects (electronic and ionic collisions, *etc.*) is illustrated by the fact that nitric oxide can be produced in the silent electronic discharge and in glow discharges at *low* temperatures. It has also been shown that the nitric oxide concentration attained depends on pressure and discharge conditions, which would not be expected for the purely thermal reaction (30). The highest concentrations are reached at about 100 mm. pressure. For ordinary air $(4N_2 + 1O_2)$ and for a nitrogen-oxygen mixture containing $4O_2 : 1N_2$, the concentrations are not the same as they should be if the system were in thermal equilibrium, being 50% greater for the latter mixture than for ordinary air under the same conditions. The law of mass action is therefore not applicable to the formation of nitric oxide in the luminous arc at small pressures. The yield of nitric oxide is also increased by increasing the frequency of the A.C. (10^7 cycles/sec.), the intensity of the nitric oxide and molecular nitrogen bands becoming greater. By increasing the frequency and decreasing the pressure it is possible in this way to double the yield of nitric oxide in the luminous arc.

The *detailed mechanism* of the electrochemical formation of nitric oxide has not yet been fully elucidated. According to electron bombardment experiments the nitric oxide formation commences at a minimum electron energy of about 17 electron volts, which according to Table 40 would roughly correspond to the ionisation energy of the nitrogen molecule. The primary

process is therefore probably the reaction

$$N_2^+ + e_0^- + O_2 \rightarrow 2NO . \qquad (34)$$

With electron energies of 22 e.volts, the formation of nitric oxide is much increased. This energy corresponds to the dissociation

$$N_2 \rightarrow N^+ + N + e_0^- , \qquad (35)$$
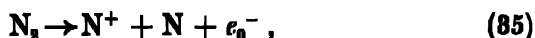
so that nitrogen ions and nitrogen atoms are available to contribute to the formation of nitric oxide. Lastly, as indicated above, it is necessary to take into account the reaction between nitrogen atoms and oxygen atoms, which, because it is strongly exothermic, only takes place by three body collisions or on the metal surface. Activation of oxygen only is insufficient to form nitric oxide at an appreciable speed as follows from the fact that if air is exposed to radiation of short wave length, ozone is formed instead of nitric oxide. The primary process in the formation of nitric oxide hence always consists in the absorption of electron energies by nitrogen.

The *formation of prussic acid* by the combination of methane and nitrogen in the luminous arc has some technical importance. The net reaction is essentially

$$2CH_4 + N_2 \rightarrow 2HCN + 3H_2 . \qquad (36)$$

Other hydrocarbons can be used in place of methane. The deposition of carbon can be avoided by the use of an excess of nitrogen. Using high frequency A.C. (10^7 cycles per sec.) and low pressures (100 mm.), n-octane, for example, yields about 120 g. of hydrogen cyanide per kwh, which corresponds to a current efficiency of about 19%. Little is at present known about the reaction mechanism. In the discharge tube the spectra of N_2^+, N^+, CH^+, C^+ and C_2 can be observed so that the primary process probably again consists of the ionisation or dissociation of nitrogen.

Finally, the reaction of pure hydrocarbons in the electric discharge must be mentioned, as they also have industrial importance. Thus acetylene can be produced from methane in the luminous arc; and higher hydrocarbons give rise to lubricating oils and motor fuels by polymerisation and hydrogenation or dehydrogenation. The kinetics of these reactions again depend

on pressure and the frequency of the A.C. used. A systematic investigation of this field has not yet been attempted.

B i b l i o g r a p h y : The Properties of Atomic Hydrogen, *Ergebn. exakt. Naturwiss.* 1927, **6**, 201; C. L. THOMAS, G. EGLOTT and J. C. MAXWELL, *Chem. Rev.*, 1941, **28**, 1; E. B. MAXTED, *Modern Advances in Inorganic Chemistry*, Oxford, 1047.

EXPERIMENTAL METHODS OF ELECTROCHEMISTRY*

1. Introduction

In the preceding chapters, description of experimental methods has been limited to the principles necessary for the understanding of the main text. In the following chapter the modern experimental methods of electrochemical research are outlined. The many references enable the original papers to be quickly and easily consulted for working details when necessary. It is hoped that this chapter will also be of particular use to the research worker.

The use of electronic techniques has recently become widespread in electrochemistry and many of the experimental methods described here require, for their full understanding, a knowledge of basic electronic principles. In order to assist the student who has not acquired such knowledge, the main part of this chapter is preceded by an elementary outline of the theory of alternating currents and thermionic valves.

(i) *Alternating Currents* [1]

The most important type of alternating current (a.c.) is that which varies sinusoidally with time, *i.e.* which may be represented by the equation,

$$i = i_0 \cos \omega t, \qquad (1)$$

where i is the instantaneous current at a time t. This equation

may be understood by considering a vector of length i_0 rotating about one end with a constant angular velocity ω.

The plot of the projection of this vector on an axis (in Fig. 82a, the y-axis) against time (t) gives a sine wave representing the variation of the current. The sine wave has an amplitude i_0 and a frequency, given by $f = \omega/(2\pi)$.

Fig. 82a. The derivation of a sine wave from the projection of a rotating vector

If an a.c. is passed through a pure (*i.e.* non-inductive, non-capacitative) *resistance* (R) the c.m.f. across the resistance is given by OHM's law as

$$E = iR = i_0 R \cos \omega t. \tag{2}$$

(Note that the usual rating of a.c. voltage *e.g.* the voltage of a mains supply, is given as the root mean square value $e = 0 \cdot 7071 \, e_0$).

If the current is passed through a pure *inductance* (L) the a.c. induces an e.m.f. in the inductance which is given by

$$E_i = -L \frac{di}{dt}. \tag{8}$$

This induced e.m.f. opposes the flow of the current and for current to pass through the inductance an equal but opposite potential difference must be applied. (Once the applied potential difference is equal and opposite to the induced e.m.f. there is no opposition to the flow of the current i because the inductance is assumed to have zero resistance. Note that the absence of opposition to the current flow does not imply an indeterminate current, because the current was fixed initially). The applied potential difference is the potential difference which may be observed across the inductance.

Using (1) the applied c.m.f. is given by

$$E = +L \frac{d}{dt} (i_0 \cos \omega t),$$

$$= -\omega L i_0 \sin \omega t,$$

$$= \omega L i_0 \sin (\omega t + \pi).$$

This equation may also be written,

$$E = \omega L \, i_0 \cos (\omega t + \pi/2) , \qquad (4)$$

which on comparison with (1), indicates that the e.m.f. is related to the current in the same way as in OHM's law (the R being replaced by ωL) but, unlike the e.m.f. across a resistance, that across an inductance leads the current by $\pi/2$ radians or 90° (Fig. 82b). This result
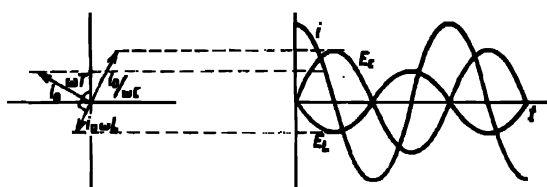
Fig. 82b. Rotating vectors and projections illustrating the potential difference across an inductance and a capacitance due to an a.c.

may also be expressed [1] by use of the operator j which denotes a 90° rotation of a vector (operation with j [2] is arithmetically equivalent to multiplication by —1). Hence equation (4) may be written

$$E = \omega L \, i_0 \cos (\omega t + \pi/2) = j \, \omega L \, i_0 \cos \omega t . \qquad (5)$$

If the a.c. is applied to a *condenser* of capacity C, the charge on the condenser at any time t will be given by

$$q = \int_0^t i \, dt ; \qquad (6)$$

and since,

$$q = C \, E ,$$

then

$$E = \frac{1}{C} \int_0^t (i_0 \cos \omega t) \, dt ,$$

$$= \frac{1}{\omega C} i_0 \sin \omega t ,$$

$$= \frac{1}{\omega C} i_0 \cos (\omega t - \pi/2) , \qquad (7)$$

or

$$E = \frac{1}{j \omega C} i_0 \cos \omega t . \qquad (8)$$

[1] See for example: B. HAGUE, *Introduction to Vector Analysis*, Methuen, London, 1930; B. HAGUE, *A.C. Bridge Methods*, Chap. II, Pitman, London, 1945; L. HARTSHORNE, *Radio Frequency Measurements*, Chapman and Hall, London, 1949.

Comparison of (7) and (1) indicates that the e.m.f. across a condenser lags behind the current by 90° (Fig. 82b).

The expressions $j\omega L$ and $1/j\omega C$ in (5) and (8), and R in (2), are known as the inductive, capacitative, and resistive *impedances*, respectively. Impedance in an a.c. circuit thus corresponds to the resistance in a d.c. circuit. Impedances (Z) in networks may be evaluated using the same laws which are used for resistances in d.c. circuits,

$$\textit{i.e.} \quad \text{in series,} \quad Z = \sum_i Z_i; \tag{9}$$

$$\text{in parallel,} \quad \frac{1}{Z} = \sum_i \frac{1}{Z_i}. \tag{10}$$

The sum of the inductive and capacitative impedances is termed the *reactance* (X), [see also Chapter I].

The above three types of impedances are limiting cases; any real circuit will contain components of each of the three, and its impedance will be the resultant of these. Consequently, the angle between the current and voltage vectors, the *phase angle*, will, in general, have values between 90° (inductive circuit) and —90° (capacitative circuit). For a pure resistance the phase angle is zero [cf. Equation (2)].

(ii) *Resonance*

An important type of circuit consists of a resistance (R), a capacitance (C), and an inductance (L) in series. From (9) the impedance is

$$Z = R + j\,\omega\,L + \frac{1}{j\,\omega\,C}, \tag{11}$$

$$= R + j\left(\omega\,L - \frac{1}{\omega\,C}\right). \tag{12}$$

This represents a vector (R) with a vector $\left(\omega\,L - \dfrac{1}{\omega\,C}\right)$ at right angles to it (indicated by the operator j). It may thus be seen (Fig. 83a) that the resultant (Z) of these two vectors has a minimum value (R) when $\omega L = \dfrac{1}{\omega\,C}$.

Hence, at constant applied potential difference a *maximum*
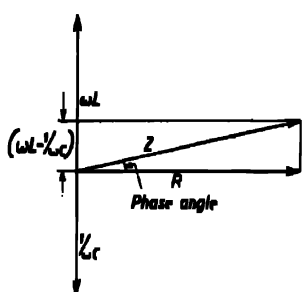
Fig. 88a. Vector diagram for a complex impedance

current is observed when this condition is imposed. The circuit is then said to be in *resonance*. Using this condition it can be seen that for given values of L and C the resonant frequency (f_r) is given by

$$f_r = \frac{\omega_r}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{1}{LC}}, \quad (18)$$

and the circuit is said to be "tuned" to this frequency. Another important type of tuned circuit is that of a condenser (capacity C) and a coil (inductance L and resistance R) in parallel. It can be shown that the resonant frequency of this circuit is again given by the expression $\frac{1}{2\pi} \sqrt{\frac{1}{LC}}$, but for this circuit it is the condition for *maximum impedance*, in contrast to the series circuit. The latter is known as an *acceptor tuned circuit* because it allows maximum current to flow at the resonant frequency, *i.e.* it "accepts" the resonant frequency, while the parallel circuit is called a *rejector tuned circuit*, because minimum current flows at the resonant frequency.

An acceptor circuit has the particularly useful property of acting as a voltage amplifier, because at resonance it has a low net impedance, although the circuit may contain two high impedances (capacitative and inductive) which effectively cancel out. Thus, if an alternating e.m.f. (E) is put across a series circuit (inductance (L), capacitance (C) and a resistance (R) in series) which is tuned to be in resonance with the applied potential difference, its impedance is R. The current flowing through the circuit is given by OHM's Law as E/R. However, this current flows through the inductance and the capacitance, which may have large (but equal and opposite) impedances, so that a potential difference much larger than that across the total circuit is obtained across the inductance; and an equal potential difference, but opposite in direction, is obtained across the capacitance: *e.g.* the voltage across the inductance is

$$E_L = i\, Z_L = \frac{E}{R}\, \omega_r\, L \, .$$

The *amplification factor* (Q) which is defined as the ratio c output to input voltage, is given by

$$Q = \frac{E_L}{E} = \frac{\omega_r L}{R} .$$ (14)
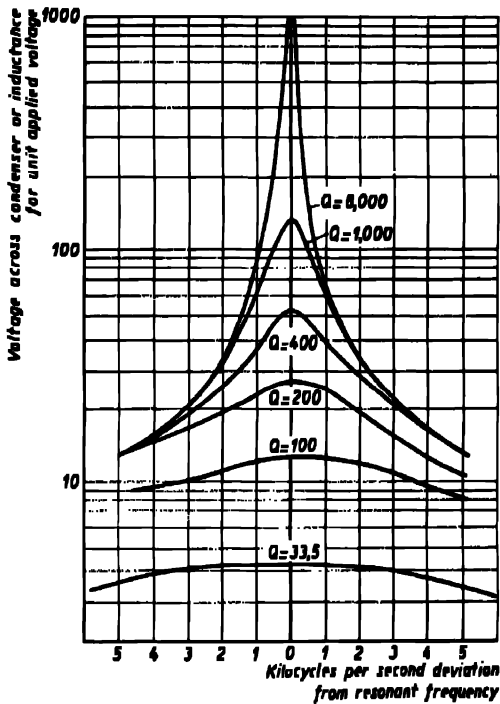
Fig. 83b. Resonance curve. Reproduced from M. G. SCROGGIE, *Foundations of Wireless*, 4th ed. (Iliffe, London, 1945)

If the current passing through the circuit (or the voltage across the condenser or inductance) is plotted against frequency, keeping the applied voltage constant, a curve of the form shown in Fig. 83b is obtained which is known as the resonance curve. A sharp maximum corresponds to a high value of Q, while a rounded maximum corresponds to a low value of Q. Since the shape of the resonance curve is a function of Q, it is possible to obtain a value of Q without knowledge of C, L and R by comparing an experimentally measured resonance curve with a diagram such as Fig. 83b.

It can be shown that the most general definition of Q for a resonant circuit is

$$Q = \frac{\text{energy stored in the system}}{\text{power loss in the system}} \times \omega_r. \qquad (15)$$

Equation (15) is of particular use for the resonant systems discussed in the following section.

(iii) *Resonant Circuits at Very High Frequencies* [1]

The use of the resonant circuits described above depends on the assumption that the current passing through the circuit at a given instant has the same value throughout the circuit. An alternating current varies from zero to its maximum value in the course of a quarter of its wavelength. Thus, the above assumption will be valid if the linear dimensions of the circuit are small compared with the quarter wavelength of the a.c. being used. Owing to the practical difficulties of making very small apparatus, the lowest wavelength practicable with ordinary resonant circuits is about 2 metres.

For a.c. of shorter wavelengths special methods must be used which have been developed from *transmission lines*. These were originally used for transmitting high frequency power (*e.g.* from a transmitter to the radiating aerial) without loss of power by radiation. It is found that the amount of power radiated by an ordinary wire increases rapidly with the frequency of the current being passed through it. For high frequencies (10^7 - 10^8 c.p.s.) power can be transmitted satisfactorily through a pair of straight parallel wires a few centimetres apart (which are known as LECHER *wires*), because the field around one wire acts in the opposite direction to that round the other at a given moment, so that the net external field is close to zero, *i.e.* radiation does not occur. For higher frequencies (up to about 10^9 c.p.s.) *coaxial conductors* form more efficient transmission lines because the field (due to the current) is completely enclosed between the inner and outer conductor. For yet higher frequencies (10^9 to $3\cdot10^{10}$ c.p.s.) more power can be transmitted through a hollow conductor than through a coaxial line (one reason for this is the power loss in the dielectric supports for the inner conductor in a coaxial line). An important feature of such hollow conductors, which are called *wave guides*, is that there is a maximum wavelength which can be transmitted through them; this is of the order of the width of the wave guide.

If some discontinuity occurs in a transmission line, some of the electro-magnetic waves are reflected (*cf.* the reflection of light when some discontinuity is present in the medium in which it is being transmitted). If the length of the line is adjusted so that the reflected wave is in phase with the original wave, standing waves are

[1] J. C. SLATER, *Micro Wave Transmission*, McGraw-Hill, New York, 1942. W. JACKSON, *High Frequency Transmission Lines*, Methuen, London, 1945. Radio Research Lab., Harvard, *Very High Frequency Technique*, McGraw-Hill, New York, 1947. B. LOVELL, *Electronics*, Pilot Press, London, 1947.

set up and the transmission line can act as a resonator. In wave guides, the required discontinuity is obtained simply by closing the end of the guide. The resulting cavity in which the standing waves occur at resonance is called a cavity resonator (*cf.* HELMHOLTZ cavity resonators for sound waves). The resonant frequency depends on the dimensions of the cavity. The power loss in such a resonator filled with air (which is approximately equivalent to a vacuum as a dielectric) is very small and, as would be expected from equation (15), the Q value is found to be large.

(iv) *The Thermionic Valve* [1]

The simplest type of valve is the *diode* which consists of two electrodes supported in an evacuated tube. One of these electrodes is heated by a low voltage current [2] until electrons are emitted thermionically (XII - 1). If a potential difference is applied across the valve so that the heated electrode is negative, electrons are attracted to the other electrode and a continuous current can flow through the valve. If the polarity of the applied potential difference is reversed, however, the electrons are attracted to the electrode at which they are produced. Under these conditions no current can pass through the valve. In this way an alternating current can be *rectified* by passing it through a diode, which allows current to pass in one direction only. It has been seen that when current is passing the heated electrode is negative; it is therefore called the cathode and the other electrode is the anode.

The diode is converted into a more useful type of valve, the *triode*, by inserting between the anode and the cathode a metal *grid* which consists of a mesh of fine wire through which electrons must pass to reach the anode from the cathode (Fig. 84). The principal advantage of a triode (and of multigrid valves) is that a very small amount of power can be used to control a much larger amount of power (obtained from the source of the cathode-anode potential difference). If the grid is at a negative

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[1] H. J. REICH, *Theory and Applications of Electron Tubes*, McGraw-Hill, New York, 1944. R. C. WALKER, *Electronic Equipment and Accessories*, Newnes, London, 1945. A. L. ALBERT, *Fundamental Electronics and Vacuum Tubes*, Macmillan, 1947. CRUFTS Electronics Staff, *Electronic Circuits and Tubes*, McGraw-Hill, New York, 1947. K. R. SPANGENBURG, *Vacuum Tubes*, McGraw-Hill, New York, 1948. L. B. ARGUIMBAU, *Vacuum Tube Circuits*, Wiley, New York, 1948.

[2] The low voltage current may pass through the electrode itself (directly heated valve) or through a separate electrode, called the filament (indirectly heated valve).

potential with respect to the cathode[1], electrons in between the grid and the cathode will tend to return to the cathode. How-
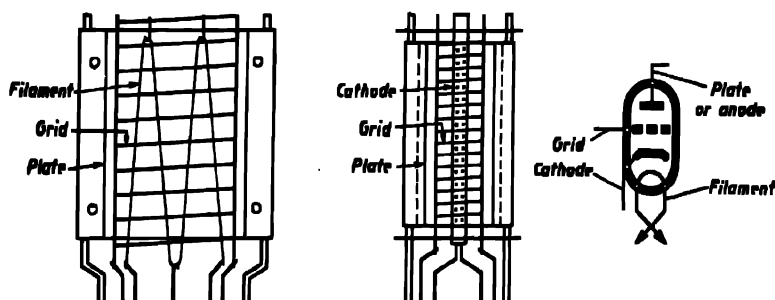
Fig. 84. The triode valve. Reproduced from H. J. REICH, *Theory and Applications of Electron Tubes* (McGraw-Hill, New York, 1944)

ever, unless the grid is at a fairly high negative potential (up to 50 volts for some valves but more often about 10 v.), a few high energy electrons will overcome the grid-cathode field and pass through the grid; although the majority of electrons (having lower energies) will be returned to the cathode. Once the electrons pass the grid they are attracted towards the anode, which is more positive than the grid and cathode; consequently a small current passes from the cathode to the anode. As the grid becomes less negative more electrons have sufficient energy to overcome the grid-cathode field and a larger current passes through the valve. The current in the circuit joining the anode and the cathode (the anode circuit) is thus a function of the potential difference between the grid and the cathode (the grid circuit); the relation is found experimentally to be linear over a considerable range for many valves. (The proportionality factor (g_m) is known as the mutual conductance and may be expressed in amp./v.). This is the basis of the use of the valve for amplification (see p. 530). Most triodes are constructed so that useful currents (1 - 50 milliamps) will flow through the anode circuit while the grid is still slightly negative with respect to the cathode. Under these conditions no electrons are attracted to the grid and no current flows in the grid circuit (in

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[1] The potentials of the electrodes of a valve are usually referred to the potential of the cathode. Thus, the 'anode potential' means the potential of the anode with respect to that of the cathode.

practice a very small current occurs due to electrons hitting the grid), hence very little power is taken from the source in the grid circuit.

For some uses (*e.g.* very high amplification, *cf.* p. 531) the triode has the disadvantage that, because of the capacitance between the anode and the grid, the larger variation of the anode potential induces variations in the grid circuit. [These would distort the potential variations originally present in the grid circuit, or even cause the valve to oscillate (see below p. 531)]. This capacitance may be reduced by placing a second grid, called the screen grid, between the original grid (control grid) and the anode. The screen grid is maintained at a constant potential close to that of the anode and acts as an electrostatic shield to prevent coupling between the control grid and the anode. This type of valve is called the *tetrode*. However, it operates unsatisfactorily if the variations of the anode potential become so large that at times the anode becomes negative with respect to the screen grid. If this occurs, some of the electrons are attracted to the screen grid (most of them have sufficient kinetic energy to pass straight through to the anode), together with secondary electrons produced at the anode by the impact of the primary electrons (Chap. XII). Thus, current will flow through the screen grid circuit. This causes undesirable effects, *e.g.* distortion of the wave form when the valve is used as an amplifier.

For many purposes the tetrode has been superseded by the *pentode* in which a third grid (the suppressor grid) is introduced between the screen grid and the anode. The suppressor grid is usually maintained at a potential close to that of the cathode and thus prevents the secondary electrons from reaching the screen grid.

(v) *The Thyratron* [1]

The thyratron, or gas-filled relay, is a triode which is filled to a low pressure (1 - 50 microns) with an inert gas, such as argon, or mercury vapour. When the grid is maintained at a negative potential with respect to the cathode, and a positive potential is

[1] S. K. LEWER and C. E. DUNHAM, *G.E.C. Journal* 1932, Nos. 2 and 3. C. E. WYNN-WILLIAMS, *Sci. J. Roy. Coll. Sci.*, 1937, **7**, 121.

applied to the anode, very little current passes. If either the grid is made less negative or the anode more positive, a critical state is reached where the number of electrons which can pass through the grid is sufficient to ionise the gas, and an arc discharge (p. 496) strikes between the anode and cathode. The ratio of the positive anode potential to the negative grid potential (both with respect to that of the cathode) at the critical condition is known as the *control ratio* (usual values are between 20 and 100). Under discharge conditions a sheath of positive ions forms round the grid so that it has no control over the discharge once it has been struck. Discharge continues until the anode potential falls to a value slightly above the ionisation potential of the gas in the valve. The energy then being supplied to the valve is insufficient to maintain the arc. The thyratron acts as a *sensitive relay*, since a very small power source can be used to supply the grid potential and the time lag for ionisation is less than 10^{-4} seconds. The current passed between the cathode and the anode is larger than that in a highly evacuated valve (about 0·1 - 0·5 amp. in a small thyratron and up to 1000 amp. in very large valves). Some provision must be made in the circuit for resetting the thyratron (*i.e.* stopping the discharge) such as interrupting the anode circuit or applying a negative pulse to the anode. The time required for deionisation is again very short (about 10^{-4} sec.).

(vi) *Basic Uses of the Thermionic Valve*

(a) *The Amplifier*

One of the most important uses of a thermionic valve is in the amplification of small voltages. The valve is normally operated under such conditions that the relation between grid potential and anode current is linear.

A change of dv_g volt in the grid potential then causes a change in $g_m\,dv_g$ amp. in the anode current (*cf.* p. 528). The same change in the anode current could be obtained by maintaining the grid potential constant and changing the anode potential by $\mu\,dv_g$ volts; the coefficient μ being known as the *amplification factor*. The change in the anode current can then be expressed by treating

the valve as a resistance of r_a ohms; *i.e.* the change in anode current is given by

$$di_a = g_m \, dv_g = \frac{\mu}{r_a} \, dv_g \,.$$

This change in anode current, however, has been calculated neglecting the influence of the external circuit. If the anode circuit contains a resistance (R) (Fig. 85), the change in
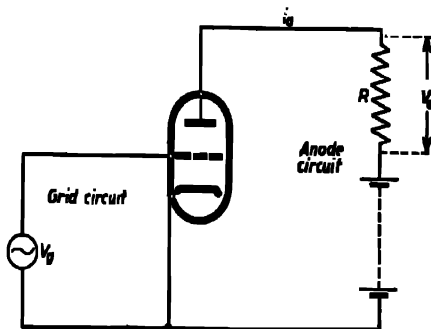
Fig. 85. Basic amplifier circuit

anode current will be $\dfrac{\mu \, dv_g}{r_a + R}$ (neglecting the resistance of the battery which is usually small). The change in the potential difference across the resistance (R) will be $\dfrac{\mu R}{r_a + R} \, dv_g$. In this way it can be seen that a valve will amplify a small potential difference applied between the grid and cathode to a potential difference $\dfrac{\mu R}{r_a + R}$ times as great, which is developed across a resistance (R) in the anode circuit.

The value of $\dfrac{\mu R}{r_a + R}$, which is known as the *stage gain*, can be largest for valves such as pentodes, because a large amplification in a triode causes coupling of the anode potential variations to the grid, as referred to above. It is usually about 100 for small pentodes and may be as low as 5 for triodes designed to carry large currents. It may be increased by increasing R, but in practice optimum working conditions are usually obtained when $R \simeq r_a$. For increased amplification several valves may be coupled together.

Owing to the rapid response of the valve, *i.e.* the low inertia of the electrons, very rapidly varying e.m.f.'s may be amplified without change in the wave form.

(b) *The oscillator*

Another important use of the valve is in the production of

sinusoidal alternating currents. It is the property of a tuned circuit such as that shown in Fig. 86a, that when the condenser is charged from any external source, the discharge through the inductance is a sinusoidal alternating current of the resonant frequency of the circuit. This is known as a *damped oscillation* because it dies away rapidly, *i.e.* the amplitude of the oscillation rapidly approaches zero.

If such a circuit is put into the grid circuit of a valve (A in fig. 86b), the damped oscillation will be amplified by the valve and an alternating potential difference will be developed across the inductance (B), which has a very much larger amplitude than that in the grid circuit. If this inductance is placed so that its

(a)   (b)
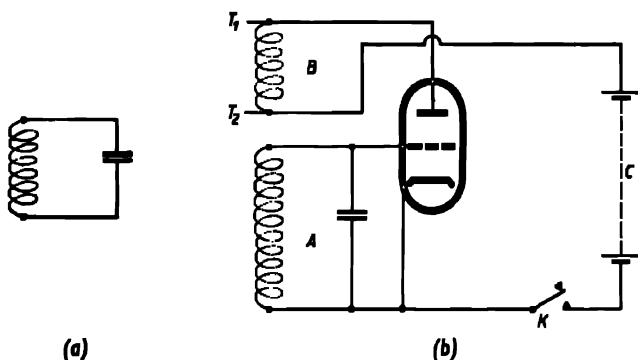
Fig. 86. Basic oscillator circuit

field interacts with that of the inductance in circuit A, this larger alternating potential difference will be induced in the grid circuit. It will then be further amplified by the valve. Thus, by a repetition of this cycle the voltage of the oscillations increases until a limiting amplitude is reached. This limit is imposed by the saturation thermionic current of the valve (see Chap. XII - 1).

The circuit shown in Fig. 86b can thus be used for a steady source of alternating current at a frequency equal to the resonant frequency of the grid circuit (A). The a.c. may be obtained from the terminals (T_1, T_2) or by means of an inductance coupled to (B). The initial charge of the condenser for the first (damped) oscillation may be obtained simply by closing the switch (K) on the high tension battery (C) or even from stray electrical disturbances in the surrounding atmosphere. Valve oscillators are

used widely [1] because they contain no moving parts to wear out, and the frequency can be varied readily by altering either the inductance or the capacitance in the tuned circuit (A).

Frequencies up to 10^7 c.p.s. can be obtained using oscillators based on the circuit described. For low frequencies, of about 10^3 c.p.s. or below, however, the components required for the tuned circuit become rather bulky and a *beat frequency oscillator* is commonly used. In this type two circuits are used, each generating high frequency oscillations, their frequencies differing by an amount equal to the low frequency desired. The output currents of the two circuits are then combined, and the desired frequency is produced as the beats between the two high frequencies. Low frequency oscillations can also be obtained in a single oscillator, by replacing the inductance-capacitance tuned circuit by a resistance-capacitance circuit [2]. *The R-C oscillator* has the advantage that it is somewhat easier to construct than the beat frequency oscillator.

(vii) *The Cathode-ray Tube*

The modern cathode-ray tube [3] is shown diagrammatically in Fig. 87. It consists essentially of a system of electrodes (A. B. C.D.E.F.) (known as an *electron ray gun*) for producing a very narrow beam of electrons, two pairs of deflector plates which can alter the direction of the beam electrostatically and a

Fig. 87. The cathode-ray tube

screen coated with a phosphor which glows for a short time
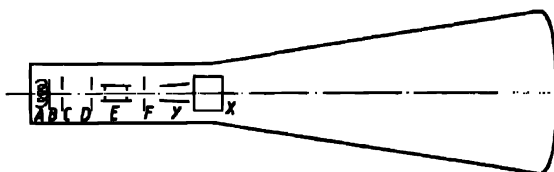
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[1] H. A. THOMSON, *Theory and Design of Valve Oscillators for Radio and Other Frequencies*, Chapman and Hall, London, 1939.

[2] See for example: F. E. TERMAN et al., Proc. Inst. Rad. Eng., 1939, **27**, 644.

[3] R. R. WATSON-WATT et al. *The Cathode-ray Tube in Radio Research*, H.M.S.O., London, 1933. J. T. MACGREGOR MORRIS and J. A. HENLEY, *Cathode-ray Oscillography*, Chapman and Hall, London, 1936. M. v. ARDENNE, *Cathode-ray Tubes*, Pitman, London, 1939. G. PARR, *The Low Voltage Cathode-ray Tube*, 2nd. Edition Chapman and Hall, London, 1943. W. WILSON, *The Cathode-ray Oscillograph in Industry*, Chapman and Hall, London, 1948.

after being struck by electrons, so that the track of the rapidly moving electron beam is visible as a continuous trace on the screen. (For a slowly moving beam the track is visible as a point of light moving, *i.e.* the quenching of the fluorescence occurs at a rate comparable to the speed of movement of the beam.) The whole system is contained in a highly evacuated tube. Electrons are produced as in a valve by the action of heat produced by a low voltage current in the filament (A), on the cathode (B). They are then accelerated towards the screen (S) by a large potential difference applied between the cathode and the first anode (D). The intensity of the beam may be controlled, as in a triode, by the grid (C). The potentials of the three anodes (D.E.F.) are adjusted so that the field between them causes all the electrons in the beam to hit very nearly the same spot on the screen (S), *i.e.* the field between the anodes acts as a system of "electron lenses" and "focusses" the electron beam. In this way a very narrow beam of electrons is sent to the centre of the screen where a spot of light is visible.

The direction of the electron beam (and consequently the position of the spot of light on the screen) may be altered by applying a potential difference between the two *deflector plates* (X or Y). The two pairs of plates are mutually at right angles so that the beam may be directed at any point on the screen. The Y plates deflect the beam in a vertical plane, and the X plates deflect it in a horizontal plane. The electron beam may also be deflected electro-magnetically by means of coils wound round the outside of the tube, but this type of oscillograph will not be considered further here. The accelerating cathode-anode voltage is usually of the order 1 - 2 kilovolts, the anodes being close to earth potential and the cathode at a large negative potential. If the cathode were earthed, the potentials applied to the deflector plates, which are normally close to earth potential, would set up a strongly decelerating field between the last anode (F) and the deflector plates; the electron beam would then be very diffuse and might not reach the fluorescent screen. The deflection of the beam, as measured by the movement of the spot on the screen, is directly proportional to the potential difference applied across the deflecting plates and inversely proportional to the accelerating

voltage. The sensitivity of a given oscillograph is usually expressed as the deflection which would occur with a potential difference of one volt across the deflecting plates, and an accelerating potential difference of one volt. It is usually between 10 and 100 cm.

The advantage of the cathode ray tube lies in the fact that the electron beam has negligible inertia (it will respond accurately to frequencies up to 10^8 c.p.s.), and also that a negligible current is drawn from the source of the voltage applied to the deflector plates.

(viii) *Applications of the Cathode-ray Tube*

On of the simplest uses for a cathode ray oscillograph is the *comparison* of the *frequencies* and *phase relationships* of two alternating potentials, by applying one potential to the X plates and the other to the Y plates. If both potentials vary sinusoidally, the movement of the electron beam is the resultant of two simple harmonic vibrations occurring at right angles to one another. A pattern, known as a LISSAJOUS *figure* (Fig. 88), is seen
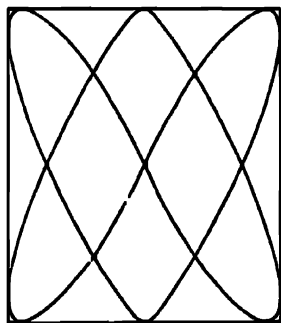
Fig. 88. LISSAJOUS figure

on the screen, which is more complex the less simple the relation between the frequency and phase angle of the two potentials. For example, a moving pattern occurs unless the quotient of the frequencies is rational. A rational frequency ratio can be determined by drawing a rectangle whose sides are tangent to the stationary pattern and parallel to the X and Y axes. The ratio of the Y to the X frequency is then the ratio of the number of points of tangency of the curve to a horizontal side, to the number to a vertical side.
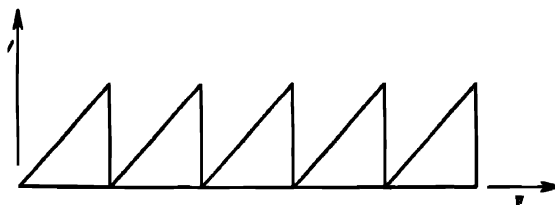
Fig. 89a. Saw-tooth wave

For most purposes, however, it is more convenient to use a voltage on the X plates such that the beam sweeps across the

screen at a constant rate, returning almost instantaneously to repeat the sweep. The varying potential difference applied to the Y plates is then shown on the oscillograph screen as a function of time. Such a voltage is known as a *time-base* voltage and is of saw tooth form (see Fig. 89a). Basically, a saw tooth wave is obtained from the charging of a condenser, which is periodically discharged. With a constant
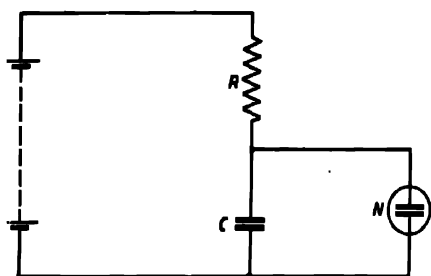
Fig. 89b. Basic time-base circuit

charging current, the voltage-time curve is very nearly linear. A very simple time base circuit is shown in Fig. 89b. The condenser (C) is charged at a constant rate controlled by the resistance (R), until the potential difference across its plates is sufficient to cause a discharge in the neon tube (N). The condenser is thus short-circuited and the potential difference across its plates falls very rapidly, until it is insufficient to maintain the discharge in the neon tube. The charging process then recommences. *In practice* [1], a more nearly constant charging rate is obtained by charging through a pentode instead of an ordinary resistance and the neon tube is replaced by the more readily controlled thyratron.

By means of a time-base, the magnitude of any voltage and its variation with time may be observed visually (or photographically). Voltage variations of about 100 v. are necessary to obtain a pattern of sufficient size but with high gain amplifiers voltage variations smaller than 1 mv. may be observed. Current variations may be observed by using the potential difference across a resistance in the circuit to be investigated. Typical electro-chemical applications of the cathode-ray oscillograph are given below (*e.g.* Conductance under high field strength p. 569; Cathode-ray Polarograph p. 585).

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[1] For practical circuits see: O. S. PUCKLE, *J. Inst. Elec. Eng.*, 1942, **89**, 100. O. S. PUCKLE, *Time Bases*, Chapman and Hall, London, 1943.

(ix) The 'Magic Eye'

A very much simplified indicator of a type similar to the cathode-ray tube is the electron ray tube or 'Magic Eye' [1]. This consists of a vertically mounted cathode surrounded by a phosphorescent target anode inclined so that it is visible from above as an annulus (Fig. 90a). Parallel to the cathode are placed control electrodes. These act as screens to the electrons, causing the segment of the anode opposite to remain dark, due to the 'shadow' of the control electrode. When the control electrode becomes more positive than the cathode, the anode-cathode field is modified and the electron beams are bent round the control electrode, i.e. the width of the shadow becomes less as the control electrode becomes increasingly positive and vice versa.

The magic eye can be used for indicating null points (when the potential difference between two parts of a circuit is zero); for example, in a potentiometer or a bridge circuit. In practice, the sensitivity is increased by use of an amplifier valve which is conveniently included in the same envelope as the magic eye, the anode of the amplifier being connected internally to the control electrodes and the cathodes connected together. The basic circuit of such a valve is shown in Fig 90b. The resistance (R) (which may be of the order of 10^5 ohm.) is inserted so that the potential difference between the magic eye anode (the fluorescent screen) and the control electrode (i.e. the anode of the amplifier) is proportional to the current passing through this resistance, i.e. the anode circuit of the amplifier valve. When the potential difference between the points (T) and (S) is zero, maximum current flows, through the
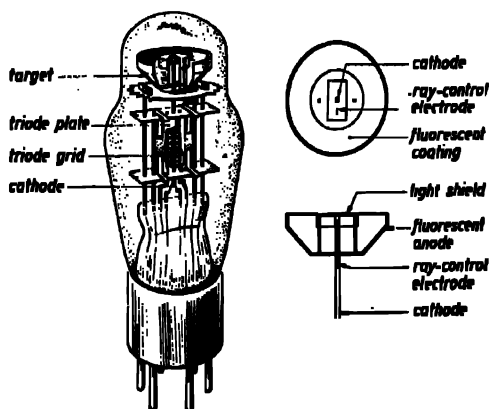
Fig. 90 a. The magic eye. Reproduced from H. J. REICH, *Theory and Application of Electron Tubes* (McGraw-Hill, New York, 1944)
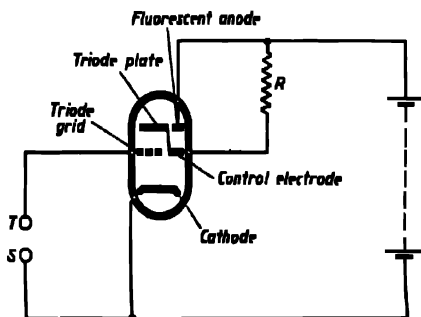
Fig. 90b. The magic eye circuit

[1] L. C. WALLER and P. A. RICHARDS, *Radio Retailing*, December, 1935, p. 47. H. C. THOMPSON, *Proc. Inst. Rad. Eng.* 1036, 24, 1270.

triode and the resistance (R). Thus there is a maximum potential difference across this resistance and hence between the control electrode and the anode of the magic eye (the former being more negative). This is the condition for maximum shadow. As the potential difference between the points (T) and (S) increases, the grid of the amplifier becomes more negative and less current flows through the valve. The resulting lower potential difference across the resistance leads to a decrease in the area of shadow observed, because the control electrode is then less negative. By connecting the two points in an external circuit to (T) and (S), the magic eye can be used to indicate when the potential difference between these two points is zero.

2. Current

(i) *Absolute Measurement* [1] (I - 4) *

The value of a current may be determined absolutely from the weight of silver deposited during a measured time in a *silver coulometer* or voltameter. (For other methods see ref. [1]).

One of the principal practical difficulties encountered in the use of a silver coulometer is due to the presence of traces of impurities in the silver anode, which on the dissolution of the latter form an 'anode slime'. Various methods [2] have been adopted to prevent these impurities from contaminating the cathodic deposit, which is weighed. A detailed study of experimental conditions for accurate silver coulometry was made by ROSA, VINAL et al. [3] who concluded (inter alia) that the solutions must not be allowed to come in contact with filter paper (as for example in the RAYLEIGH coulometer).

The *coulometer* developed *for accurate work* has a platinum bowl, which contains the electrolyte, as the cathode while the silver anode is suspended in the centre. The separation between anode and cathode is achieved by use of either a carefully prepared porous pot (RICHARDS [2] loc. cit.), or a glass disc with a glass cylinder ground into it (SMITH [2]). The glass cylinder is kept lowered except during the actual electrolysis. Great care is required in the preparation of the silver nitrate for the electrolyte, an almost exactly neutral salt being required to ensure that pure silver is deposited. The anodes are the best electrolytic silver and the silver removed is usually replated from the bowl after each experiment.

* These reference numbers refer to the connected topic in earlier chapters.

[1] A. GRAY, *Absolute Measurements in Electricity and Magnetism*, 2nd. Edition, Macmillan, London, 1921. F. A. LAWS, *Electrical Measurements*, 2nd. Edition, Mc Graw-Hill, New York, 1938. P. VIGOREUX and C. E. WEBB, *Electric and Magnetic Measurements*, Chap. II, Blackie, London, 1946.

[2] Lord RAYLEIGH, *Phil. Trans.*, 1884, A 175, 411. F. E. SMITH, *Report of Nat. Phys. Lab.*, 1910, p. 82. T. W. RICHARDS, *J. Am. Chem. Soc.*, 1915, 37, 20.

[3] E. S. ROSA, G. W. VINAL et al., *U.S. Bureau of Stds. Bull.*, 1913, 9, 151, 493; 113, 10, 425, 475.

The silver coulometer described is unsatisfactory for currents greater than one·ampere and for such currents, and for general purposes when extreme accuracy is not required, the *copper coulometer* is used since it is much simpler in operation. A study of this coulometer was made by MATTHEWS and WARK [1] using a cylindrical copper anode and a cylindrical platinum wire gauze cathode. The electrolyte is copper sulphate solution; and for low currents the addition of alcohol appears to improve the deposit. At currents greater than 8 amps it is necessary to rotate the cathode. The results are accurate to about 0·1%. It may also be noted here that the *hydrogen-oxygen coulometer*, which is direct reading, is accurate to about the same order if pure potassium or sodium sulphate is used as the electrolyte [2].

(ii) *Subsidiary Measurements*

For laboratory purposes it is usually inconvenient to use absolute methods of current measurement. Results of a similar order of accuracy can be obtained with calibrated subsidiary instruments, such as the galvanometer, which are well described in textbooks of practical physics [1 p. 528, 3].

A useful method, often used for measurements of low currents, is that of passing the current through a calibrated resistance the potential difference across which is measured with a potentiometer (section 7).

3. Heats of Solution and of Dilution (III - 4)

The classical "can" calorimeter [4] has been used recently for *approximate measurements*. ZELLHOEFER and COPLEY [5], for measurements of relatively large heat changes, used a calorimeter

[1] H. P. MATTHEWS and L. W. WARK, *J. Phys. Chem.*, 1931, **35**, 2340; *cf.* A. L. Marshall, *Trans Faraday Soc.* 1925, **21**, 297.

[2] R. A. LEHFELDT, *Phil. Mag.* 1908, (4), **15**, 614. J. J. LINGANE, *Faraday Soc. Discussion*, 1947, **1**, 203.

[3] A. W. SMITH, *Electrical Measurements in Theory and Application*, McGraw-Hill, New York, 1948.

[4] M. P. E. BERTHELOT, *Thermochimie*, Gautier-Villars, Paris, 1897. H. P. J. J. THOMSEN, *Thermochemistry*, Longmans Green, London, 1908.

[5] G. F. ZELLHOEFER and M. J. COPLEY, *J. Am. Chem. Soc.*, 1938, **60**, 1343.

in which mixing took place in a vessel immersed in diethyl phthalate in a DEWAR flask. The temperature rise of the diethyl phthalate was observed with a BECKMANN thermometer. Owing to the relatively large mass which undergoes the temperature change and the limited accuracy (10^{-3} °C.) of the temperature measurement, this method is only suitable for studying large heat changes to an accuracy of a few percent. More accurate types of calorimeter also using DEWAR flasks but with resistance thermometers have been described by VOLD, by PITZER, and by SOUTHARD [1].

In the *adiabatic calorimeter* developed by RICHARDS *et al.* [2] accuracy is greatly increased by reducing the heat exchange between the calorimeter and its surroundings to a minimum. The temperature of the calorimeter surroundings is kept very nearly equal to that of the calorimeter itself, using either manual control (more usual for rapid processes), or automatic (in slower processes) control [3]. This is most conveniently accomplished by means of a differential thermocouple (one junction in the calorimeter and one in the jacket), or a differential resistance thermometer with the two resistance wires in adjacent arms of the measuring bridge [4].

The most accurate determinations of heats of dilution have been carried out using a *differential adiabatic calorimeter* (see especially LANGE and ROBINSON [5], and GUCKER, PICKARD and PLANCK [6]) in which the temperature difference is observed between two calorimeter vessels identical in all respects except that in one the reaction being studied proceeds while the other acts as a standard. This highly sensitive apparatus was developed primarily to test the predictions of the heat of dilution of strong electrolytes made by the DEBYE-HÜCKEL theory (*cf.* question 6, Chapter V).

[1] R. D. VOLD, *J. Am. Chem. Soc.*, 1937, **59**, 1515.   K. S. PITZER, *ibid.*, 1937, **59**, 365.   J. C. SOUTHARD, *Ind. Eng. Chem.* (*Ind. Ed.*), 1940, **32**, 442.

[2] T. W. RICHARDS *et al.*, *J. Am. Chem. Soc.*, 1909, **31**, 1275, *etc.*

[3] *Cf.* R. FRICKE, *Z. f. Naturforschung*, 1947, **20**, 39.

[4] *e.g.* J. M. STURTEVANT, *J. Phys. Chem.*, 1941, **45**, 127.

[5] E. LANGE and A. L. ROBINSON, *Chem. Revs*, 1931, **9**, 89.

[6] L. T. GUCKER, H. B. PICKARD and R. W. PLANCK, *J. Am. Chem. Soc.*, 1939, **61**, 459.
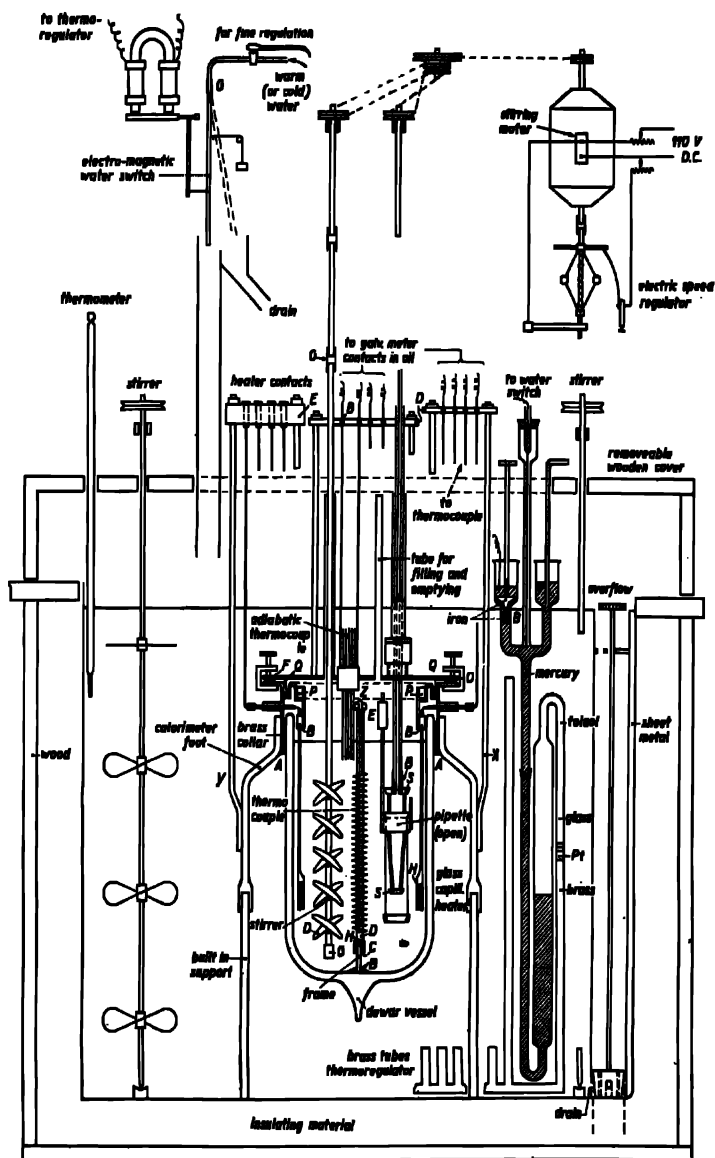
Fig. 91. Adiabatic calorimeter for heats of dilution of electrolytic solutions.
Reproduced from *Chem. Rev.*, 1931, 9, 97

Use of the equation given in problem V–6 (or the more exact form [1]) shows that the heat of infinite dilution of a $0 \cdot 1M$ solution of a 1-1 valent salt would be expected to be of the order of 100 cal.g.mol. $^{-1}$ of salt. However, experimentally both the initial amount of solution and the degree of dilution are limited by the dimensions of the calorimeter so that the dilution must be carried out in a number of stages. Thus, the heat changes observable are of the order $0 \cdot 1$ cal. to $0 \cdot 001$ cal., corresponding to temperature changes of 1000 to 1 microdegree.

The *differential calorimeter* used by LANGE and co-workers [1 p. 540] (Fig. 91) consisted of anunsilvered DEWAR vessel of about two litres capacity, divided symmetrically by a thermally insulating partition in which was mounted a multiple junction thermocouple. The latter was made up of about 1000 individual iron-constantan thermocouples mounted with alternate junctions on opposite faces of the partition. This, together with a sensitive mirror galvanometer, gave a maximum deflection of 1 mm. for 10^{-7} °C. Each section of the calorimeter was provided with identical dilution pipettes, heating elements for calibration and stirrers. The DEWAR vessel was immersed in a water bath the temperature of which could be maintained constant within $0 \cdot 0002$ °C by means of a large mercury regulator controlling the addition of warm or cool water to the bath (preferable to the use of an electric heater which has too great a lag). A 24 element thermocouple built into the calorimeter vessel lid enabled the temperature difference between the calorimeter and the bath to be observed and controlled. The calorimeter was calibrated by passing known quantities of electricity through the heating elements inside the DEWAR flask. In this way the effective water equivalent of the system and the heat conductivity constant were accurately determined [2]. The latter is a measure of the rate at which the calorimeter gains or loses heat from its surroundings. Errors due to the dilution pipettes being at a slightly lower temperature than that of the calorimeter liquid were eliminated by opening both pipettes at once, one containing the solution being studied and the other liquid of the same composition as that in the two halves of the calorimeter.

[1] E. LANGE and L. J. MEIXNER, *Physik. Z.*, 1929, 30, 670, using the theory of T. H. GRONWALL, V. K. LaMer and V. K. SANVED, *ibid.*, 1928 29, 358.

[2] For calculations on heat losses see: H. C. DICKINSON, *Bull. U.S. Natl. Bur. Stds.*, in 1915, 11, 184. W. P. WHITE, *The Modern Calorimeter*, New York, 1928. J. M. STURTEVANT in A. WEISSBERGER, *Physical Methods of Organic Chemistry*, Interscience, New York, 1946.

4. Dielectric Polarisation (III)

(i) *Dielectric Constants* [1]

The measurement of dielectric constants is important both intrinsically (*e.g.* for use in the interionic attraction theory) and for the calculation of dipole moments (see p. 552). The measurements on pure substances are not difficult and the results may be stated with some accuracy, but measurements of dielectric constants of electrolytic solutions involve special difficulties as a result of the appreciable conductance of the solution. Results obtained for the dielectric constants of electrolytic solutions using different methods are extremely discordant, and no final assessment of the most satisfactory method can be given at the present time.

(a) *The bridge method* (See also Section 6)

The type of WHEATSTONE bridge circuit described in Chapter I can be used for the comparison of capacities [2] and for measurement of dielectric constant, since the capacity of a condenser of given dimensions is proportional to the dielectric constant of the medium separating the plates. For *media of low conductance* (non-electrolytes) the modern radio frequency bridge operating at a frequency between 10^4 and 10^8 c.p.s. is capable of considerable accuracy. The highest accuracy is obtained using a *substitution method* [3]. The bridge is first balanced (for balance in an a.c. bridge not only the potential but the phase of the potential must be the same at opposite corners of the bridge) with the unknown impedance forming one arm. This is then replaced by standard components, such as a calibrated variable resistance in parallel with a calibrated variable condenser, and by adjusting these components the bridge is returned to balance. The impedance of the standard components is then equal to that of the unknown which they have replaced. In this way possible errors such as coupling

[1] C. A. D. CLARK, *Fine Structure of Matter*, part. II. Chapman and Hall, London, 1941. C. J. F. BÖTTCHER, *Theory of Electric Polarisation*, Elsevier, Amsterdam 1952.
[2] *Cf.* B. HAGUE, *A.C. Bridge Methods*, Pitman, London, 1945.
[3] But *cf.* K. W. WAGNER and A. WERTHEIMER, *Physik. Z.*, 1912, **13**, 868.

with surrounding objects or inaccuracy in the components in the remainder of the bridge are eliminated. A bridge capable of high accuracy in measurements of systems of low conductance has been described recently by SCHUPP and MECKE [1].

For systems of *high conductance* the bridge method, like the tuned circuit methods, is subject to two errors which greatly reduce its accuracy.

(1) The electrical circuit equivalent to the test cell is uncertain. Experimentally the circuit is measured either as Fig. 92a or Fig. 92b. For these circuits to behave identically electrically it
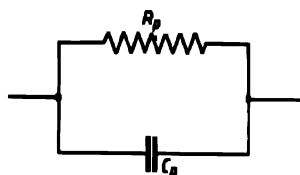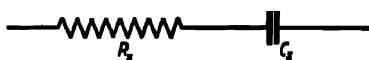
Fig. 92a.   Fig. 92b.

Equivalent circuits

can be shown by equating the vector potential difference [*cf.* equations (2), (8), (9) and (10)] across the two circuits that,

$$R_s = \frac{1}{1/R_p + \omega^2 C_s^2 R_p} \,, \tag{16}$$

and

$$\frac{1}{C_s} = \frac{\omega^2 C_p}{1/R_p^2 + \omega^2 C_p^2} \,. \tag{17}$$

If the resistance of the solution is large, $C_s \simeq C_p$, with the result that the choice of equivalent circuit is not important. However, for electrolytic solutions R_p is small and this approximation cannot be made. The actual equivalent circuit is almost certainly more complex than those considered above, but the measurement of the current-voltage relationships across the cell impedance (as in an a.c. bridge) provides insufficient information for the calculations of the parameters of a more complex circuit.

(2) The passage of an alternating current through an impe-

[1] R. L. SCHUPP and R. MECKE, Z. *Elektrochemie*, 1948, **52**, 40.

dance of this type distorts the sine wave so that the normal a.c. theory is not strictly applicable.

Measurements of the impedance of a cell containing a dielectric of appreciable conductance, and the dielectric constant calculated therefrom, must be regarded at best as approximations. These considerations apply to the resonance and heterodyne beat methods (see below) as well as to the bridge method.

Bridge methods have been used for the measurement of dielectric constants of electrolytic solutions of specific conductance up to about 10^{-3} mhos at frequencies of about $10^6 - 10^7$ c.p.s.[1]. From equation (17) it may be seen that the higher the frequency the more the capacitative part of the impedance affects its behaviour *i.e.* at very high frequencies $C_p \rightleftharpoons C_s$ even if R_p is small.

(b) *Tuned circuit methods*

(1) T h e   R e s o n a n c e   M e t h o d : The capacity of a condenser can be measured using the resonance condition (Eq. 13). When an unknown capacity is placed in parallel to the
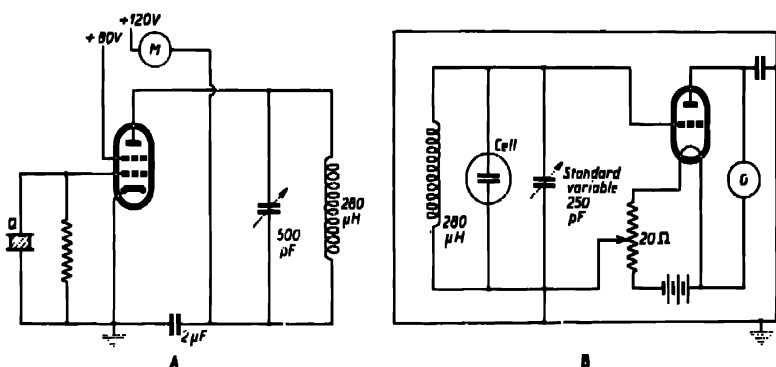
Fig. 98. Circuit for measurement of dielectric constant.
Reproduced from R. J. W. Le Fèvre, *Dipole Moments* (Methuen, London, 1938)

standard variable capacity of a circuit initially in resonance, the adjustment which has to be made to the standard condenser in order to reinstate the condition of resonance is equal to the capacity of the unknown.

[1] M. Wien, *Ann. Physik*, 1931, 11, 429. O. Neese, *ibid.*, 1931, 8, 920. E. Fischer, *Physik. Z.*, 1935, 18, 585.

This method, like the bridge method, is suitable for low conductance media; the maximum specific conductance permissable is 10^{-4} or 10^{-3} mho. A simple circuit is described by LE FEVRE [1]. This consists of an oscillator (A) Fig. 98 (the PIERCE circuit) in which the tuned circuit is replaced by a quartz crystal resonator (Q) [*]. The latter controls the frequency of oscillation within much closer limits than an inductance-capacitance circuit. Certain crystals (quartz, tourmaline) have the property, known as piezo-electricity, that when they are subjected to mechanical strain, electric charges appear on the surfaces. Conversely, if a potential difference is applied across the crystal, mechanical strains appear. If an alternating potential difference is applied the crystal vibrates. The amplitude of this vibration is very small unless its frequency coincides with the natural vibration frequency of the crystal, when it becomes very much larger. In this way the crystal acts as a resonator and may be used for stabilising the frequency of a valve oscillator.

The circuit (B) is the resonating circuit. The current flowing through the tuned circuit is measured by amplifying the potential difference across the standard condenser and passing the anode current of the valve through a milliammeter. A maximum deflection on this indicates that the resonant frequency of circuit (B) is identical with that being generated by circuit (A) to which (B) is coupled inductively.

The resonance method is discussed in detail by HARTSHORNE [2]. It suffers from the same disadvantage as the bridge method for conducting media, but has been applied to electrolyte solutions up to $0.01N$ [3] using
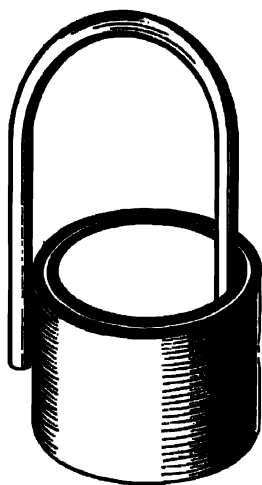
Fig. 94.
Total immersion resonator.
Reproduced from
J. WYMAN, *Phys. Rev.*,
1930, **35**, 623

[1] R. J. W. LE FEVRE, *Dipole Moments*, Methuen, London, 1938.

[*] L. HARTSHORNE, *Radio Frequency Measurements by Bridge and Resonance Methods*, Chapman and Hall, London, 1940.

[3] P. WALDEN *et al.*, *Z. physikal. Chem. A.*, 1925, **116**, 261. R. T. LATTEY and W. G. DAVIES, *Phil. Mag.*, 1932, **13**, 7, 444.

frequencies of about 10^8 c.p.s. For dilute electrolyte solutions of conductance up to 100 times that of pure water, WYMAN [1] used a small fixed resonating system which could be entirely immersed in the medium under investigation. This system consisted of two coaxial cylinders (Fig. 94) joined by a support containing a hot wire element in contact with one junction of a thermocouple by means of which the current through the system was observed. The frequency of an oscillator was varied until maximum current was observed in the resonating circuit which was immersed in the medium. Frequencies between 10^6 and 10^8 c.p.s. were used. From the value of the resonant frequency the capacitative part of the impedance can be calculated. By comparing the capacity when the resonator is in the medium being investigated with that when the resonator is in air, the dielectric constant is obtained.

(2) The Heterodyne Beat Method: This is similar to the resonance method in that the tuning property of an inductance-capacitance circuit is used. The circuit here forms the tuned circuit of an oscillator, the frequency of which is determined by the parameters of the network. The capacity of an unknown can then be measured by a substitution method, as described above. The frequency of the oscillator is determined by means of the heterodyne beat method. The signal from the oscillator is combined with that of a standard (crystal controlled) oscillator and at small frequency differences an audible beat note is produced. As the difference between the frequencies decreases the note becomes lower, and when complete silence is attained the two frequencies are identical. If the test cell is put into parallel with the standard condenser of the tuning circuit, the net capacity is the sum of the cell capacity and that of the standard condenser [cf. equations (8) and (10)]. Thus, for this oscillator to again generate signals of the same frequency as that of the standard oscillator, the capacity of the standard condenser must be decreased by an amount equal to the capacity of the cell. From the cell capacity the dielectric constant may be calculated, as described for the bridge and resonance methods [1,p. 148].

This method is particularly adaptable to measurements in the

[1] J. WYMAN, *Phys. Rev.*, 1930, **35**, 623.
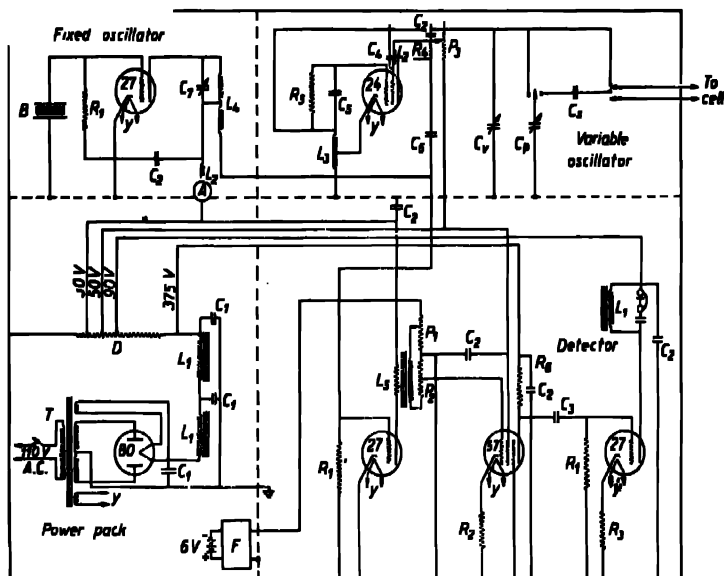
Fig. 95. The heterodyne beat method.

A = milliammeter; B = mounted quartz crystal; D = type-D Electrad Truvolt 10,000-ohm resistor; T = Thordarson T-6012 high-power transformer; F = 1000-cycle tuning fork hummer; $R_1 = 10^6$ ohms; $R_2 = 1300$; $R_3 = 1800$; $R_4 = R_5 = 10^5$; $R_6 = 25,000$; $P_1 = P_3 = 25,000$; $P_2 = 500,000$; $C_1 = 8$ microfarads; $C_2 = 2$; $C_3 = 0.0025$; $C_4 = 0.005$; $C_5 = 0.001$; $C_6 = 5\,\mu\mu f.$; $C_7 = 100$; $C_P = 1100$ (variable precision condenser); $C_V = 1000$ (variable auxiliary condenser); $C_8 = 100$; $L_1 = 30$-henry choke; $L_2 = $ radio frequency choke; $L_3 = 51$ turns of No. 26 wire wound on an octahedral form 8·6 cm in diameter, of which 20 turns are in the grid circuit; $L_4 = 92$ turns of No. 26 wire on a similar form in the plate circuit and 12 turns below them as the pickup; $L_5 = $ audiotransformer with a 1 : 6 ratio. Reproduced from A. WEISSBERGER, *Physical Methods of Organic Chemistry*, 1st ed., Vol. II (Interscience, New York, 1948)

gas phase owing to the high accuracy obtainable (in non-con-ducting systems), which is necessary because the dielectric constant of a gas differs little from unity.

A circuit of the type used by STRANATHAN, and also by SMYTH [1], is shown in Fig. 95. The constant frequency oscillator output and the output from the variable oscillator are fed into the detector circuit where the signal is amplified and observed with the earphones. For more sensitive detection (*e.g.* in measurements of gases) the beat frequency of the two oscillators is combined with an exactly 1000 c.p.s. signal from a tuning fork oscillator (F). The variable oscillator can then be adjusted

[1] C. T. ZAHN, *Phys. Rev.*, 1924, 24, 400. H. E. WATSON, *Proc. Roy. Soc.*, A, 1934, 143, 558. J. STRANATHAN, *J. Chem. Phys.*, 1938, 6, 395. C. P. SMYTH et al., *J. Am. Chem. Soc.*, 1938, 55, 453; 1942, 64, 2820, *J. Chem. Phys.*, 1941, 9, 352.

to a position of minimum noise; when its frequency differs from that of the fixed oscillator by exactly 1000 c.p.s. For the highest accuracy it is necessary to thermostat the oscillating circuits, particularly the crystal (B). The maximum conductivity for which this method can be used is the same as that for the resonance method.

Cells for use with the above methods are based on the coaxial cylindrical form introduced by SAYCE and BRISCOE[1] (Fig. 96). Modifications of this cell are described in detail in the literature cited in this section. Allowance must be made for the capacitance of the leads, which will remain constant for a given system.

(c) *Standing wave methods*

The length (λ) of standing waves on LECHER wires (see p. 526) is given by

$$\lambda = \frac{1}{f \sqrt{\varepsilon \mu}}, \qquad (18)$$

where f is the frequency of the waves, and μ the permeability of the surrounding medium. Hence, the dielectric constant (ε) of a medium may be determined by measuring the wavelength of the oscillation

Fig. 96. SAYCE—BRISCOE cell. Reproduced from LE FEVRE, *Dipole Moments* (Methuen, London, 1938)

when the wires are in air (or in a vacuum) (λ_0), and in the medium under investigation (λ),

$$\varepsilon = \frac{(\lambda_0)^2}{\lambda^2}, \qquad (19)$$

if it can be assumed that the magnetic permeability of the medium does not differ from that of air. Two methods of this type were proposed by DRUDE[2] for electrolytic solutions, but were quite

[1] L. A. SAYCE and H. V. A. BRISCOE, *J. Chem. Soc.*, 1925, **127**, 315.

[2] P. DRUDE, Z. *physikal. Chem.*, 1897, **23**, 267.

unsatisfactory until the introduction of electronic oscillators to replace the earlier unreliable spark oscillator [1]. The measurements were made at a wavelength of about 1 metre i.e. $8 . 10^8$ c.p.s., and with solutions of concentration about $0.005N$, or less. This method is unsatisfactory for electrolytic solutions at high concentrations because the damping (cf. page 532) of the oscillations on the wires becomes too great, i.e. the field round the wires cannot be maintained in a conducting medium.

(d) Very high frequency methods

It was shown above that according to equation (17) more accurate results for dielectric constants could be obtained if a very high frequency a.c. is used. Recent developments in radar technique have made centimetre waves (frequency $10^9 - 3 . 10^{10}$ c.p.s.) available for this work [2].

HASTED, RITSON and COLLIE [3] have used waveguides (see p. 526) for the measurement of dielectric constants of electrolytic solutions. One method used was a resonance method, analogous to those described above. The ordinary tuned circuit was replaced by a cavity resonator which, as was mentioned on p. 527, has a very high value of Q, because of the low power loss in the circuit. When a very small quantity of a dielectric which had an appreciable conductance was introduced into the resonator, the power loss in the resonator increased sharply, i.e. the value of Q decreased. By measuring this change in Q it was possible to calculate the dielectric constant of the substance introduced into the resonator. In practice, it was found that a suitable change in Q is obtained if the electrolytic solution is introduced into a capillary fixed axially in the cylindrical wave guide resonator. The value of Q was obtained by measuring the resonance curve (cf. Fig. 89b).

[1] H. HELLMANN and M. ZAHN, Ann. Physik, 1926, **81**, 711, etc. P. WALDEN et al., Z. physikal. Chem., 1927, **129**, 388, etc. M. T. DRAKE, G. W. PIERCE and M. T. DOW, Phys. Rev., 1930, **35**, 613. DEVOTO, Gazz. chim. ital., 1931, **61**, 783. E. PLOTZE, Ann. Physik, 1933, **18**, 5, 288. J. G. MALONE, A. L. FERGUSON and L. O. CASS, J. Chem. Phys., 1933, **1**, 836, 842. M. ROVER, Ann. Physik, 1934, **21**, 320.
[2] W. JACKSON, Faraday Soc. Discussion, 1946, **42A**, 91. Papers on pp. 101 to 169 in Faraday Soc. Discussion on Dielectrics, 1946, 42A. F. HORNER, T. A. TAYLOR, R. DUNSMUIR, T. LAMB and W. JACKSON, J. Inst. Elec. Eng., 1946, **93**, part. III, 53.
[3] J. B. HASTED, D. M. RITSON, and C. H. COLLIE, J. Chem. Phys., 1948, **16**, 1.

The authors claim that the dielectric constant obtained is accurate to within about 4%. Within this accuracy no deviation from the dielectric constant of pure water was observed until the solution became more concentrated than $0.5N$. This is in agreement with the small change found in the dielectric constant in some of the measurements made by the methods described above which appear satisfactory up to $0.01N$. Thus, measurements using centimetre waves are available only for solutions more concentrated than $0.5N$. Consequently, no direct comparison is possible with other methods, and no reliable results are available for the region $0.01 - 0.5N$.

(e) *Force methods*

The dielectric constant of a medium may be obtained directly by measuring the force between two known charges immersed in the medium and using COULOMB's law,

$$P = \frac{q_1 q_2}{\varepsilon r^2} . \tag{20}$$

Since this relation does not depend on the conductance of the medium, this type of measurement should be particularly suitable for electrolytic solutions.

The most used method is based on the deflection of a small conducting ellipsoid suspended between two plates across which a low frequency alternating potential difference is applied. The deflection is measured by means of a mirror attached to the suspension (*cf.* the mirror galvanometer). The theory of the method was developed by FURTH [1] who showed that the deflecting force is given by

$$D = A \, \overline{E^2} \, \varepsilon \sin 2 \, \theta , \tag{21}$$

where A contains constants characteristic of the apparatus, $\overline{E^2}$ is the mean value of the square of the potential difference across the plates, and θ is the angle between the major axis of the ellipsoid and the lines of force of the applied field. Other workers [2]

[1] R. FURTH, *Z. Physik*, 1924, **22**, 98.

[2] R. PECHOLD, *Ann. Physik*, 1927, **83**, 427.   O. MILICKA and A. SLAMA, *ibid.*, 1931, **83**, 5, 663.   W. ORTHMANN, *ibid.*, 1931, **9**, 5, 537.   G. FISCHER and W. D. SCHOFIELD, *ibid.*, 1936, **25**, 450.   W. J. SHUTT *et al.*, *Trans. Faraday Soc.*, 1934, **30**, 893, *ibid.*, 1938, **34**, 468. *Proc. Roy. Soc.* A., 1940, **175**, 234.

have developed the method for use in electrolytic solutions using frequencies between 50 and 10^6 c.p.s. The limiting factor at high electrolyte concentrations is the JOULE heating effect and the highest concentration at which measurements have been made is 0·1N. Accurate results are, however, difficult to obtain using FURTH's method and the results do not compare well with those obtained by the other methods.

A second force method, in which the force between two plates immersed in a dielectric was compared with that between two plates in a standard dielectric, was developed by CARMAN [1]. The results obtained were unsatisfactory owing to the heating of the solution, although the method appears promising for electrolytic solutions.

(ii) *Dipole Moment from Dielectric Constant* [2] (III - 7)

In order to obtain the dipole moment from dielectric constant measurements it is necessary to separate the orientation polarisation from the other contributions to the total polarisation (see III - 7, equation 86).

(a) *The refractivity method*

At very high frequencies ($> 10^{11}$ c.p.s.) the applied field changes direction so rapidly that the dipoles have insufficient time to orient with the field. Consequently the contribution of the orientation polarisation to the total polarisation becomes zero. If the dielectric constant were measured under these conditions the total polarisation at about 10^{11} c.p.s. could be compared with that at low frequencies, the difference between the two being the orientation polarisation. However, measurements in this frequency range are experimentally very difficult. At even higher frequencies ($> 10^{14}$ c.p.s.) the contribution of the atomic polarisation also becomes zero for the same reason. These frequencies

[1] A. P. CARMAN, *Phys. Rev.*, 1924, 24, 396; 1927, 30, 924. C. C. SCHMIDT, *ibid.*, 1927, 30, 925.

[2] C. P. SMYTH, *Dielectric Constant and Molecular Structure*, Chem. Catalog. Co. New York, 1931. P. DEBYE, *Dipole Moment and Chemical Structure*, Blackie, London, 1931. R. J. W. LE FEVRE, *Dipole Moments*, Methuen, London, 1938. C. P. SMYTH, in A. WEISSBERGER, *Physical Methods of Org. Chem.*, Interscience, New York, 1946.

are in the visible region, and the dielectric constant due to electronic polarisation of a medium may be readily obtained from its refractive index (n) using a relation due to MAXWELL,

$$\varepsilon = n^2. \tag{22}$$

In order to evaluate the *electronic polarisation* the static dielectric constant is required and is obtained by extrapolation to infinite wavelength (*i.e.* zero frequency) of a series of measurements of the refractive index in the visible region. After subtracting this result from the total polarisation, the remainder is the sum of the orientation and atomic polarisations.

Owing to the experimental difficulties in the frequency range 10^{11} - 10^{14} c.p.s. the *atomic polarisation* cannot be measured and it is often taken to be a constant small fraction (5 - 15%) of the electronic polarisation. However the extrapolation of the refractive index to infinite wavelength leads to a correction of the same order as that due to the atomic polarisation but opposite in sign. For this reason the refractive index obtained using the sodium D line is often used directly for the calculation of the polarisation, the result being assumed to include the contributions of both the electronic and the atomic polarisation. This is then subtracted from the total polarisation, calculated from low frequency measurements, to obtain the orientation polarisation.

(b) *The temperature method*

From Equation (III - 36) it may be seen that only the orientation polarisation is dependent on temperature. By making measurements of the dielectric constant at various temperatures and plotting total polarisation against $1/T$, the dipole moment can be obtained from the slope of the line ($4\pi N \mu^2/9 k$).

(c) *Ebert's method*[1]

The orientation polarisation may also be evaluated approximately with the aid of measurements in the solid state, in which, owing to the rigid lattice, the contribution of this term will be very small. The total polarisation obtained under these conditions may thus be taken as the sum of the electronic and atomic contributions. Using this value together with measurements in the gas state at the same temperature, the dipole moment may be evaluated as in the refractivity method.

[1] L. EBERT, *Z. physikal. Chem.*, 1924, **113**, 1.

(iii) *Dipole Moments of Substances in Solution*

The derivation of the DEBYE (equation III, 36) is made assuming that the molecules are distributed randomly in the absence of an applied field, or that interaction between the molecules can be neglected. This condition is fulfilled for gases at low pressure only, but in practice it is found that the equation can be used for dilute solutions of *polar molecules* in non-polar solvents. The total molecular polarisation is an additive property, and that of the solute may be found from the difference between that of the solution and that of the pure solvent. The actual measurement is, however, not as simple as this because of the tendency for the association of dipoles which may increase or, more usually, decrease the apparent moment (see Chapter III). Association is not important for a non-polar solvent, and may be eliminated for the solute by extrapolating the apparent total polarisation to infinite dilution. The dipole moment is then calculated by one of the methods described above.

(iv) *Methods for the Determination of Dipole Moments not Depending on Dielectric Constant*

The following methods, though less accurate than those so far described, provide valuable confirmatory results, because they are completely independent of the above methods.

(a) If a field is applied perpendicularly to a *beam of polar molecules* travelling through a vacuum the beam is broadened in proportion to the dipole moments of the molecules (*cf.* the STERN-GERLACH experiment [1]). Only semi-quantitative results have been obtained and the method is experimentally difficult [2].

(b) If a field E is applied to a volume V_0 of a gas, the gas decreases in volume by ΔV due to *electrostriction* according to the equation,

$$\frac{\Delta V}{V_0} = \frac{E^2}{2\,kT}\left(a + \frac{\mu^2}{3\,kT}\right).$$

The method is difficult because of the small volume changes involved (10^{-4} cc.[2])

(c) DEBYE [4] showed that the *absorption of energy by a dielectric* is proportional to the square of the dipole moment of the molecules therein. Thus, the moment could be calculated from the heating effect of a high frequency a.c.

5. Optical Methods (IV - 4).

The important application of spectrophotometry to the determination of true dissociation constants was discussed in section

[1] O. STERN and W. GERLACH, Z. *Physik*, 1021, 1, 249.
[2] I. ESTERMANN in P. DEBYE, ref. 42. R. FRAZER, *Molecular Rays*, Cambridge, 1931. R. FRAZER, *Molecular Beams*, Methuen, London, 1937.
[3] O. E. FRIVOLD, *Physikal. Z.*, 1921, 22, 603.
[4] P. DEBYE, *Trans. Faraday Soc.*, 1934, 30, 689.

IV - 4. The fundamental measurement involved is that of the intensity of light. Absolute measurements of intensity of light are difficult, and all practical methods depend on the comparison of two intensities; they differ in the type of spectra used and in the method of comparison.

(i) *Absorption Spectra* [1]

For the *absolute measurement of extinction coefficients* monochromatic light must be used; a close approximation to this is obtained by using a spectrograph with a narrow slit and high dispersion, or more satisfactorily by using a line source and a monochromator. By varying the wavelength of the light a complete absorption curve for a region of the spectrum can be obtained for each concentration of the solution. If the system being studied is a simple ion-undissociated molecule equilibrium, change in the total concentration causes no shift of the absorption bands but only a change in intensity due to the relative change of concentration of the two absorbing components (*cf.* equation IV - 20). At one particular wavelength the extinction coefficient remains constant *i.e.* all the curves of extinction coefficient against wavelength cross at the same point which is called the isosbestic point. It can be shown that the existence of an isosbestic point provides a criterion for an equilibrium of this type.

The spectrophotometric measurements most often employed are those in which a band of light (*i.e.* only approximately monochromatic light) is used; a *relative extinction coefficient* is thus obtained which is a mean value for this range of wavelength. When the range of wavelengths used approaches that of the whole visible spectrum the method is termed colorimetry.

In all modern methods of absorption spectrophotometry the

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[1] T. R. P. Gibb, *Optical Methods of Chemical Analysis*; McGraw-Hill, New York, 1942. W. R. Brode, *Chemical Spectroscopy*; Wiley, New York, 1943. R. E. Burk and O. Grummit, *Major Instruments of Science and their Application to Chemistry*; Interscience, New York, 1945. W. West, in A. Weissberger, *Physical Methods of Organic Chemistry*; Interscience, New York, 1946. E. A. Braude, *Ann. Rep. Chem. Soc.*, 1945, **42**, 108. G. Kortüm, *Kolorimetrie und Spektralphotometrie*, 2nd. edition; Heidelberg, 1948. G. F. Lothian, *Absorption Spectrophotometry*; Hilger and Watts, London, 1949.

light from the source is split by an optical system into two
beams [1]; one of which is passed through a cell containing the
solution with an unknown concentration of the substance under
investigation, the other may pass either directly to the measuring
instrument, or through a solution of the same substance at a
known concentration or through a variable iris diaphragm, a
rotating sector, a wedge shaped block of grey glass, a filter or
other optical device to vary the intensity of the beam by a known
amount. The measuring instrument may be the eye, a photo-
graphic plate or a photocell. *Visual methods* depend on the
adjustment of the intensity of the second beam until it is equal
to that of the first; the standard solution, rotating sector and iris
diaphragm are particularly suitable. The use of a standard solution
for comparison is preferable to that of optical and mechanical
devices [2] because the same substance is reducing the intensity
of both beams, *i.e.* the mean extinction coefficients of both
are equal, and the measurements are independent of the nature
of the light used. The maximum accuracy obtainable by visual
methods is about 0·5% of the measured extinction.

The same type of comparison can be accomplished *photo-
graphically* by observing points of equal blackening on the same
plate, which correspond to light of equal intensity. The grey wedge
is particularly suitable for use with a photographic method because
the light transmitted has a range of intensities corresponding to
the varying thickness of the wedge. A cell with a length varying
in steps (Echelon cell) containing standard solution may be used
in a similar manner. In a more difficult absolute method the
intensities of two beams are compared directly by measuring the
densities of the images produced on a photographic plate, using
a *microdensitometer*. In this instrument a powerful narrow beam
of light is projected through the plate, and the intensity of the
transmitted light measured by means of a photoelectric cell. The
recording may be manual, but automatic instruments are also in
use, in which the movement of the photographic plate is synchro-

[1] V. HENRI, *Physikal. Z.*, 1913, 14, 515.   G. SCHEIBE, F. MAY and H. FISCHER,
Ber., 1924, 57, 1331.   F. TWYMAN, *Trans. Opt. Soc.*, 1931/2, 33, 1.   H. v. HALBAN,
G. KORTÜM and B. SZIGETI, *Z. Elektrochem.*, 1936, 42, 628.

[2] G. KORTÜM and J. GRAMBOW, *Z. angew. Chem.*, 1940, 53, 188.

nised with the movement of the strip on which the intensities are recorded.

In *photoelectric photometry* the eye is replaced as a measuring instrument by the photocell. The principle of the measurement remains the same, but the accuracy increases to 0·01% of the measured extinction if the conditions are controlled [1]. The increased accuracy is due to the fact that the photocell reacts to the absolute difference of intensity dI whereas the eye is sensitive only to the relative difference of intensity dI/I. The most accurate results are obtained by using two photocells, one in each beam connected in a balanced circuit; equal intensity is indicated by a null deflection of an electrometer or valve voltmeter. This method eliminates the effect of variations of the light source. Alkali photocells of the gas-filled type are used because of their high sensitivity, but they are difficult to use experimentally [2].

Colorimetric methods are essentially the same but a much broader band of light is employed; a standard comparison solution is always used and the nature of the light used is not important. Photoelectric colorimetry can be simply carried out by titrating one solution with solvent until its extinction becomes equal to that of the other [3].

(ii) *Fluorescence Measurements* [4]

The dissociation constants of fluorescent electrolytes can be obtained from fluorescence measurements. These do not differ from absorption spectra measurements in practical details, but only in the nature of the source of the observed light. In measurements of dissociation constants it is important to keep

[1] G. Kortüm and H. v. Halban, Z. *physik. Chem.* (A), 1934, **170**, 212; (B), 1936, **33**, 248.

[2] G. Kortüm, Z. *angew. Chem.*, 1941, **54**, 442; *Chem. Technik*, 1942, **15**, 167.

[3] A. Ringbom, Z. *analyt. Chem.*, 1938, 115, 332, 402; 1939, 116, 104. G. Kortüm and H. Schöttler, Z. *angew. Chem.*, 1940, **61**, 204.

[4] J. A. Radley and I. Grant, *Fluorescence Analysis*, 3rd. edition; Chapman and Hall, London, 1939. P. Pringsheim and M. Vogel, *Luminescence*; Interscience, New York, 1943.

the total concentration less than that in which "concentration quenching" occurs (at high concentrations the molecules begin to lose energy by collision more rapidly than by fluorescence, and the intensity of fluorescence is no longer proportional to the concentration).

(iii) *Raman Spectra* [1]

For some electrolytes the extinction coefficients of the ions and of the molecule are insufficiently specific to enable an accurate calculation of the true dissociation constant. For some of these the RAMAN spectra provide an alternative method. The essential principle of comparing intensities of RAMAN lines is the same as that used in absorption spectrophotometry and a comparison solution is always used for accurate results [2]. Since the RAMAN spectrum consists of scattered light it has a low intensity. Therefore, a high intensity line source with no continuous emission is necessary, together with a spectrograph

Fig. 97. RAMAN cell and illuminator

R = ellipto-cylindrical reflector.

C = RAMAN cell blackened on shaded parts.

L = glass tube for liquid filter (*e.g.*, sodium nitrate solution).

F = glass filter to supplement L for isolation of single line.

H = mercury vapor arc in air-cooled box.

S = spectrograph.

[1] G. B. B. M. SUTHERLAND, *Infra Red and Raman Spectra*; Methuen, London, 1935. J. H. HIBBEN, *The Raman Effect and its Chemical Applications*; Reinhold, New York, 1939. R. E. BURK and GRUMMIT, ref. 1 p. 555.

[2] O. REDLICH and R. ROSENFELD, *Monatsh.*, 1936, 67, 223; R. DALMON, *Compt. rend.*, 1940, 211, 472; O. REDLICH and J. BIGELEISEN, *J. Am. Chem. Soc.*, 1943, 65, 1883; O. REDLICH, E. K. HOLT and J. BIGELEISEN, *ibid.*, 1944, 66, 13; E. BAUER and M. MAGAT, *Mém. Serv. Chim. l'Etat*, 1944, 31, 113, 171; O. REDLICH, *Chem. Rev.*, 1946, 39, 333; J. CHÉDIN and S. FENÉANT, *Compt. rend.*, 1947, 224, 1424.

of large aperture [1]. A high dispersion is also necessary to separate
the RAMAN spectrum from the exciting line. Maximum intensity
of the scattered light relative to that of the exciting light is obtained
at right angles to the latter, so that an apparatus similar to that
shown in Fig. 97 is used. The arc source (H) (usually a quartz
mercury arc) is contained in a metal box with a slit in the lid.
Above this are placed suitable filters (F) for isolating the required
line, one of which is a glass tube containing liquid (L), acting as
a cylindrical lens which focusses the beam at the centre of the
RAMAN tube (C). The latter is cylindrical and has the end
remote from the spectrograph drawn out and blackened to
prevent reflections from the glass entering the spectrograph.
The other end has a black iris diaphragm. On the upper surface
of the tube is placed a hemicylindrical piece of aluminium
foil (R) to reflect light back into the tube. In order that glass
optical systems may be used the light employed is usually in
the visible range. Owing to the low intensity of RAMAN lines the
method is difficult experimentally and is less accurate than
that of absorption spectrophotometry.

6. Ionic Migration

(i) *Conductance of Electrolytic Solutions* [2]

(a) *Electrical circuit* (I - 3, VI)

As mentioned in Chapter I, it is necessary to use an a.c. bridge
method for the measurement of the conductivity of electrolytes
in order to eliminate the effect of polarisation at the electrodes.
The chief difficulty encountered in the application of the *alternating
current bridge* to accurate conductance measurements is the ambi-
guity as to the quantity which is measured. This arises as a result

[1] J. R. NIELSEN, *J. Opt. Soc. Am.*, 1930, **20**, 701. D. H. RANK, R. T. PFISTER and
P. D. COLEMAN, *ibid.*, 1942, **32**, 390; 1943, **33**, 31. R. F. STAMM, *Ind. Eng. Chem.*
(*Anal. Ed.*), 1945, **17**, 318.

[2] C. W. DAVIES, *Conductivity of Solutions*, Chapman and Hall, London, 1930; L.
EBERT, *Handbuch der Experimentalphysik*, 1932, **12**, 1; J. REILLY and W. N. RAE,
Physico-Chemical methods, 2nd. Edition, Methuen, London, 1933; T. SHEDLOVSKY,
in A. WEISSBERGER, *Physical Methods of Org. Chem.*, Interscience, New York, 1946.

of "stray coupling" between different parts of the bridge circuit, which allows the passage of the alternating current through undesired paths [1]. *Inductive (electromagnetic) coupling* may occur between the oscillator and the detector causing some a.c. to pass directly from the oscillator to the detector thus vitiating the balance of the bridge. Similarly, *capacitative (electrostatic) coupling* mutually between parts of the bridge circuit and between the bridge circuit and surrounding objects, effectively causes the introduction of capacities into different parts of the circuit and leads to an erroneous position of balance.

The first step in eliminating such effects is to make them more accurately defined, *i.e.* to eliminate variable effects due, for example, to coupling between movable objects such as the operator. For example, the arms of the bridge may be individually *screened*. This may not reduce the bridge—earth capacitance but it makes it a more definite quantity. Electromagnetic interaction may be reduced by shielding with a material of high permeability which intercepts the magnetic lines of force, or, more simply, by separating the components with high inductances; *e.g.* the oscillator may conveniently be placed at a distance from the remainder of the bridge. The most common and satisfactory method of eliminating earth capacitance effects is that known as the *Wagner earth* [1]. The use of this device may be illustrated for a simple bridge A B C D (Fig. 98). If the bridge is balanced in the normal way, it is assumed that the absence of current through the detecting instrument indicates that the corners of the bridge to which it is connected (C D) are at the same potential. This assumption will not be valid if there is coupling between the connections to the detector, or between C and D and earth, since some of the current which should flow through the detector will then leak around it and a false balance will be obtained. An example of such coupling is the electrostatic coupling between headphones and an earthed
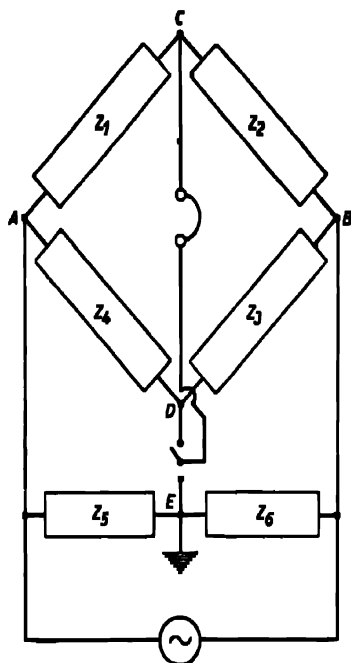
Fig. 98. The Wagner earth

[1] B. Hague, *A.C. Bridge Methods*, Pitman, London, 1947.
[1] K. W. Wagner, *Elek. Z.*, 1911, **32**, 1001.

observer. If an auxiliary network Z_5 Z_6 is included, all earth capacitance effects may be eliminated. The bridge is first balanced with the switch in position D then with it in position E; these operations being repeated until perfect balance is obtained in the two networks, i.e. Z_1, Z_2, Z_3, Z_4 and Z_1, Z_2, Z_5, Z_6. It may then be readily seen that the points C and D are at the same potential as E, namely earth potential, so that no current can flow from C and D through earth capacitances to any neighbouring body. Also, any earth capacitances from the points A and B are effectively connected in parallel with Z_5 and Z_6 respectively when the switch is in position D and are thus removed from the main bridge circuit. The chief difficulty of the device is the rate of convergence of the two readings to perfect balance (which is more rapid the better the design of the bridge). A complete theory of earthing devices for bridges was given by OGAWA [1].

The resistors used for bridges must be wound non-inductively in order that they approximate closely to pure resistances. The variable condensers used are usually of low capacity, about 100 p.f. [*] They must be of good quality, but need not be precision standard condensers.

The *power source* in modern work is a valve oscillator producing a pure sine wave. The frequency used is about 1000 c.p.s. which is sufficiently high to eliminate

$C_1 - 260\ MMFD$
$C_2 - 15$ „
$C_3 - 25$ „
$C_4 - 365$ „
$R_1 - 40\ Ohms$
$R_2 - 2$ „
$R_3, R_4, R_5, R_6 - 10,000\ Ohms$

G.R. 578-B

OSC.
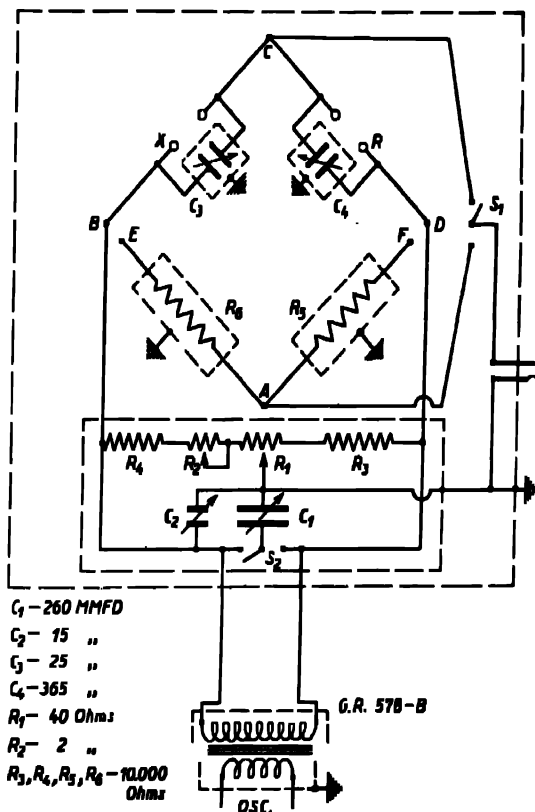
Fig. 99. Modern conductance bridge
Reproduced from *J. Am. Chem. Soc.*, 1940, **62**, 93

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[*] 1 p.f. (picofarad) $= 10^{-12}$ farads.

[1] K. OGAWA, *Elect. Lab. Min. Comm.*, Tokyo, Res. 1929, No. 254, p. 1; 1930, No. 227, p. 1. See also, A. V. ASTIN, *Bureau Stds. J. Res.*, 1938, **21**, 425.

polarisation at the electrodes; higher frequencies would lead to an increased effect of stray capacitances since a capacitative impedance decreases with increase of frequency [Equation (8)]. A variable frequency is useful since the bridge may be checked by means of measurements at different frequencies. The elimination of polarisation may be confirmed if the conductivity does not vary with frequency.

The most satisfactory *detector* for these frequencies is the earphone, usually combined with a simple valve amplifier (see page 580). For greater sensitivity, an acceptor tuned circuit may be included in the amplifier since this selects the required frequency, and tends to eliminate other frequencies which might interfere with the estimation of the position of minimum sound [1].

Bridges useful for accurate measurement of the conductance of solutions have been described by JONES and JOSEPHS and by SHEDLOVSKY [2]. A *typical modern* modification is that of LUDER [3] (Fig. 99). This bridge has an almost constant sensitivity over a range of measurement from 10^3 to $2 . 10^5$ ohms.

In this apparatus the a.c. was supplied by a degeneratively tuned oscillator in which the harmonic content may be readily reduced to the order of 0·1%. A two stage amplifier and telephones were used for detection. This permitted an adjustment to balance of one or two parts per million in a quiet room. For greater sensitivity a three stage amplifier was used, but it was necessary to include a simple tuned circuit in the final stage to eliminate noise due to the valves. Using this circuit no mains hum or harmonics could be detected.

When the resistance of the unknown becomes *greater than about* 10^6 *ohms* the bridge method becomes insensitive, and a *direct method* appears to be the only one possible. It consists essentially in measuring the current passed through the cell when a known potential difference exists across it. At such high resistances the current passed is extremely small, and the polarisation at platinised platinum electrodes becomes negligibly small in comparison with the ohmic drop across the solution. This method was used by FUOSS and KRAUS [4] who applied a potential of 150 v. across

[1] D. J. G. IVES and R. W. PITTMAN, *Trans. Faraday Soc.*, 1948, **44**, 644.

[2] G. JONES and R. C. JOSEPHS, *J. Am. Chem. Soc.*, 1928, **50**, 1049. T. SHEDLOVSKY, *ibid.*, 1930, **52**, 1793.

[3] W. F. LUDER, *ibid.*, 1940, **62**, 89.

[4] R. M. FUOSS and C. A. KRAUS, *ibid.*, 1933, **55**, 21; R. M. FUOSS, *ibid.*, 1938, **60**, 451.

a cell in series with a galvanometer of maximum sensitivity $4 \cdot 10^{-10}$ amp./cm. Thus, with a cell of cell constant 0·02 a liquid of specific conductance of $5 \cdot 10^{-14}$ mho cm.$^{-1}$ could be investigated. At resistances of about 100,000 ohms, these authors found that results obtained using the d.c. method agreed to within 1% of those obtained using the a.c. bridge method (*cf.* BENT and DORFMAN [1]).

Some measurements have also been made using so-called "non-polarisable" electrodes such as $Ag|AgCl$ and $Hg|Hg_2SO_4$[2], although these electrodes are polarisable to some extent. After subtraction of the back e.m.f. of the cell from the applied e.m.f., the conductance of the solutions obtained was in good agreement with that from the normal a.c. method. This method is limited to use with electrolytes which take part in the electrode reaction.

(b) *The conductance cell*

The main requirements for a conductance cell are that it should be of a relatively insoluble glass (*e.g.* Pyrex or Hysil), the electrodes should be rigidly supported and the cell constant should be such that, for the solutions to be used, the cell resistance will be from $10^3 \cdot 10^4$ ohms. If the cell resistance is lower, errors due to polarisation tend to increase because of the higher current passing through the cell. If the resistance is high, the current leakages in the insulation become significant. It is also important that the electrode leads, and any filling tubes containing solution, should be separated from each other as far as possible to reduce the electrostatic coupling between them (*cf.* the equivalent electrical circuits shown in Fig. 100).

Cells of the pipette type were found by PARKER [3] to exhibit a variation of the cell constant with the resistivity of the solution used (*The "Parker Effect"*). JONES and BOLLINGER [4] showed that

[1] H. E. BENT and M. DORFMAN, *ibid.*, 1935, 57, 1924.
[2] J. N. BRØNSTED and R. F. NIELSON, *Trans. Faraday Soc.*, 1935, 31, 1478.
L. V. ANDREWS and W. E. MARTIN, *J. Am. Chem. Soc.*, 1938, 60, 871.
[3] H. C. PARKER, *ibid.*, 1923, 45, 1366, 2017. See also: M. RANDALL and G. N. SCOTT, *ibid.*, 1927, 49, 630. F. A. SMITH, *ibid.*, 1927, 49, 2107.
[4] G. JONES and D. M. BOLLINGER, *ibid.*, 1931, 53, 411.
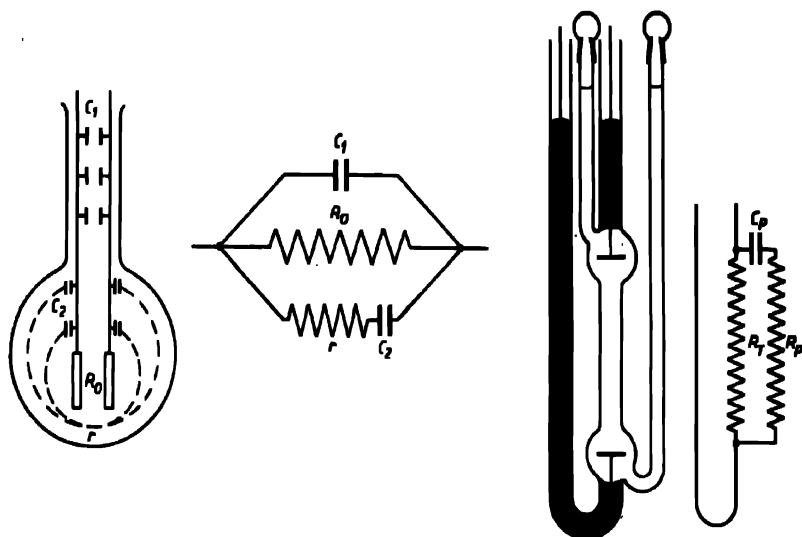
Fig. 100. Errors in conductance cells. Reproduced respectively from A.Weissberger, *Physical Methods of Organic Chemistry*, 1st ed., Vol. II (Interscience, New York, 1948) and from *J. Am. Chem. Soc.*, 1931, **53**, 431

this was due to stray coupling between the cell and the filling tubes. *Modern conductance cells* (Fig. 101) are based on designs by JONES and BOLLINGER [4p.563] (a) (for highly conducting solutions) and by SHEDLOVSKY [2p.502] (b) (for poorly conducting solutions such as protein solutions).

The electrodes are of stout platinum and are usually platinised to reduce polarisation. A velvety black coating suitable for this is obtained by using a platinising solution containing about 3% chloroplatinic acid and about 0·02% lead acetate. After cleaning the cell, *e.g.* with aqua regia, and washing, the solution is introduced into the cell and platinisation carried out, using an e.m.f. of about 4 v. which is reversed every minute until a thick coating is obtained.

For *dilute solutions* the polarisation is less significant, and since absorption of the electrolyte by the finely divided platinum may appreciably alter the concentration, it is necessary to use *grey platinum electrodes*. These are produced by heating platinised electrodes to a dull redness. These electrodes may also be used for solutions (especially non-aqueous solutions) containing sub-

stances which decompose in the presence of platinum black,
although it may be necessary to use smooth platinum electrodes.
With the latter, polarisation
effects may be eliminated by
making measurements at various
frequencies and extrapolating
to infinite frequency. A plot
of resistance against the re-
ciprocal of the square of the
frequency is used for this extra-
polation [1].

(a)

(b)
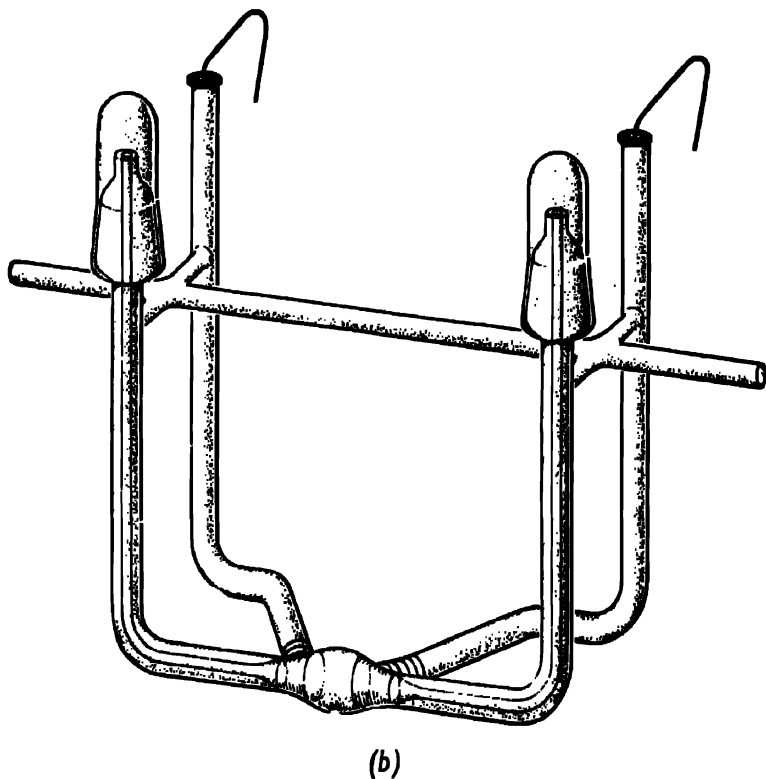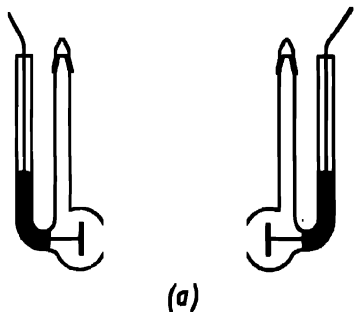
Fig. 101. Modern conductance cells. Reproduced from A. WEISSBERGER, *Physical
Methods of Organic Chemistry*, 1st ed., Vol. II (Interscience, New York, 1948)

[1] W. A. TAYLOR and S. F. ACREE, *J. Am. Chem. Soc.*, 1916, **38**, 2415.

(c) *Temperature control*

The degree of temperature control necessary depends on the precision required of the conductance measurements. For accuracies of the order of 1 in 10^4 control within 0·01 °C. is necessary. *Oil thermostats* are preferred to those containing water because the lower conductance and dielectric constant of the oil enables the magnitude of leak currents through the bath to be reduced.

(d) *Preparation of water for conductance measurements*

Stills for the production of pure water are generally made from quartz, block tin or pyrex glass, and well seasoned. Water is distilled from alkaline permanganate solution to oxidise traces of organic matter; and if air is not excluded, the distillate contains carbon dioxide This water is called *equilibrium water* and has a specific conductivity of about 10^{-6} mho cm.$^{-1}$ at 18 °C. By exclusion of atmospheric carbon dioxide the conductivity of the water can be readily reduced to about $6 . 10^{-8}$ mho cm.$^{-1}$ at 18 °C., *i.e. conductance water*. Stills for the production of conductance water have been described by KRAUSS and DEXTER, VOGEL and JEFFERY, THIESSEN and HERRMANN [1] *(inter alios)*. The carbon dioxide content may be reduced by distilling in a current of carbon dioxide free air and by fractionally condensing the steam, the first fraction being virtually carbon dioxide free. [*]

(ii) *Conductance under Limiting Conditions of Field Strength and Frequency*

(a) *Conductance under conditions of high field strength* [3] (V - 4)

The principal difficulty in these measurements is the large

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[*] KOHLRAUSCH and HEYDWEILER [2] redistilled water 42 times under reduced pressure in apparatus seasoned for ten years in water, and obtained water of conductivity $4·1 . 10^{-8}$ mho cm.$^{-1}$ at 18 °C.

[1] C. A. KRAUS and W. B. DEXTER, *J. Am. Chem. Soc.*, 1922, 44, 2468. A. I. VOGEL and G. H. JEFFERY, *J. Chem. Soc.*, 1931, 1201. P. A. THIESSEN and K. HERRMANN, *Z. Elektrochem.*, 1937, 43, 66.

[2] F. KOHLRAUSCH and A. HEYDWEILER, *Wied. Ann.*, 1894, 53, 234, *Z. physikal. Chem.*, 1894, 14, 317.

[3] H. FALKENHAGEN, *Electrolytes*, Oxford, 1934. H. C. ECKSTROM and C. SCHMELZER, *Chem. Rev.*, 1939, 24, 367.

Joule heating effect in the solution. This has been overcome by the use of a high field of very short duration (*i.e.* by a d.c. pulse method). The magnitude of the heating effect may be realised by considering that the rise in temperature, when a field of 10^5 v./cm. is applied for 10^{-6} sec. to a solution of specific conductance 10^{-4} mho, is about 0·24 °C (assuming the solution to have unit specific heat and density).

Ideally, a square pulse is desirable, *i.e.* the field strength should reach its maximum value instantaneously and decay to zero instantaneously (full line in Fig. 102). In practice, however, both the build up and decay require a finite time and the field strength varies continuously with time (dotted line in Fig. 102). The mean field strength must then be calculated by integration. The pulse is usually produced by charging a condenser with the current induced in the secondary winding of an induction coil when the primary circuit is opened, until the condenser discharges across a spark gap. This is known as the *single spark method*.
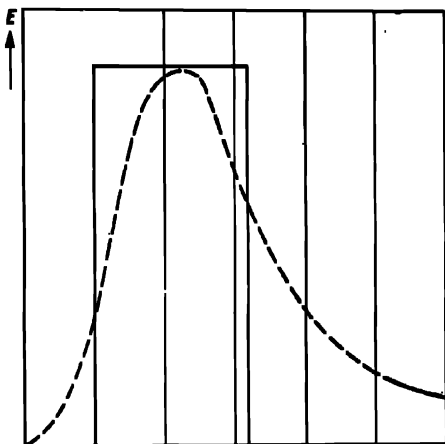
Fig. 102. Ideal pulse and actual form of pulse obtained. Reproduced from H. Falkenhagen, *Electrolytes*, transl. by R. P. Bell (The Clarendon Press, Oxford, 1932)

In the original method of Wien[1], the mean current passed during a pulse in a circuit consisting of a condenser, an inductance, a spark gap and a resistance (Fig. 103) was compared with that passed under the same conditions except that the resistance was replaced by a conductance cell. The current was determined by measuring the heating effect of the current induced in a circuit coupled to the main circuit. The field strength could be varied by adjusting the length of the spark gap.

Field strengths of up to $5 \cdot 10^5$ v./cm. were obtained, and the results were accurate, to about ±1%. The inaccuracy was mainly due to the irreproducibility of the spark

M. Wien, *Ann. Physik*, 1924, **73**, 101.

potential and the accuracy was improved to about 0·1% by MALSCH and WIEN [1], who used a circuit enabling the comparison between the known and unknown resistances to be made at the same time and not consecutively. The essential circuit

(I) is the same as that of the first method except that the two resistances, together with coupling inductances, are connected in parallel. The currents flowing through R_1 and R_2 are compared using a *barretter bridge* (II). The pulse currents in the circuits containing R_1 and R_2 are each induced into barretter
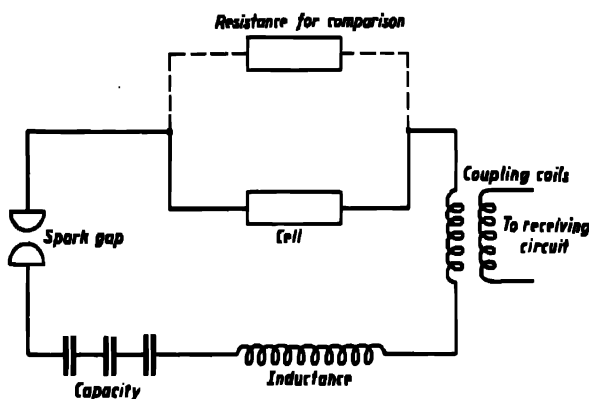
Fig. 103. WIEN's first method *

circuits. The latter consist of an inductance M for coupling, a large condenser K and a barretter lamp O (MALSCH and WIEN used ordinary incandescent lamps). The current in the barretter circuit heats the filament of the lamp and changes its resistance which is thus related to the intensity of the current flowing in it. These currents are confined to the barretter circuit by means of inductances (chokes), and the net resistance of the circuit may be measured using ordinary bridge methods. MALSCH and WIEN used a symmetrical bridge which was balanced when equal
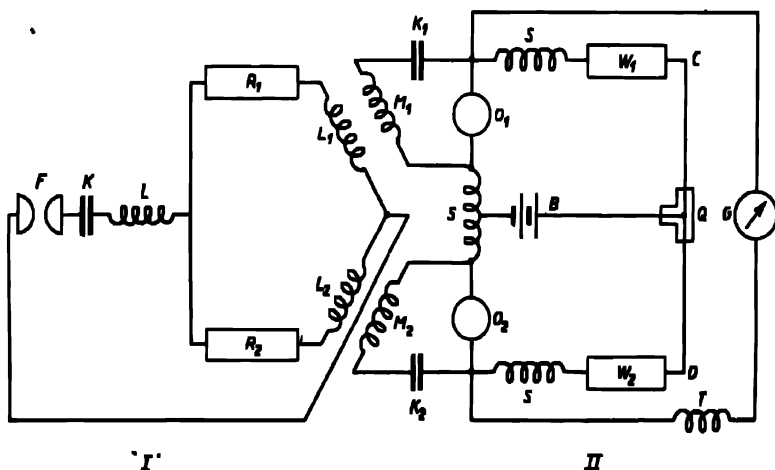
Fig. 104. WIEN's second method *

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* Reproduced from H. FALKENHAGEN, *Electrolytes*, transl. by R. P. BELL (The Clarendon Press, Oxford, 1932).

[1] J. MALSCH and M. WIEN, *ibid.*, 1927, **83**, 305.

currents were induced into the two barretter circuits. The resistance R_1 was adjusted until the bridge was balanced. Then, since equal currents were flowing through R_1 and R_3, the value of R_3 was equal to that of R_1. It is thus a null method and is consequently more accurate than the first method.

Both methods of WIEN consist, essentially, in the measurement of the mean resistance of the solution during a very short pulse of electricity and the correlation of this with a mean field strength. To calculate the latter, the wave form of the pulse must be known because the field strength actually changes continuously. The mean field strength may then be calculated by integrating the field strength over the time interval and dividing by the time interval. Investigations on the effect of high field strength on conductance in non-aqueous solutions have more recently been carried out by FUOSS et al.[1]. A more conventional type of bridge was used with which field strengths up to about $1 \cdot 5 \cdot 10^5$ v./cm. were obtained.

The laborious integration is avoided by an oscillographic method due to FUCKS[2], in which the potential across the cell is directly compared with that across a known resistance-capacity network. Fig. 105. The actual curve of the variation of the potential difference across the cell with time is observed on the oscillograph screen and photographed. In this way, the potential difference across the cell and that across the standard can be compared at a given instant so that instantaneous values of the field strength and conductivity may be obtained, thus avoiding the necessity for calculating mean values. The method is, however, less accurate than the single spark method because of errors in the measurement of the image on the photograph, although the results confirm those obtained by WIEN's method.
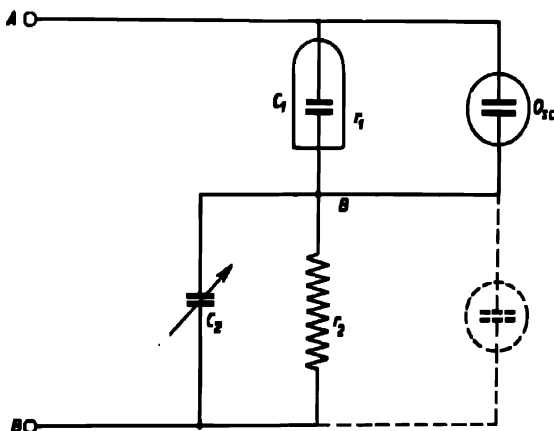
Fig. 105. FUCKS' oscillographic method. Reproduced from H. FALKENHAGEN, *Electrolytes*, transl. by R. P. BELL (The Clarendon Press, Oxford, 1932)

(b) *Conductance under conditions of rapidly alternating field*

The first accurate results for the conductance of electrolytes measured with *high frequency currents* were obtained by SACK et al.[3]

[1] R. M. FUOSS et al., *J. Am. Chem. Soc.*, 1939, **61**, 2047; 1940, **62**, 1720.

[2] W. FUCKS, *Ann. Physik*, 1932, **12**, 306.

[3] H. SACK et al., *Physikal. Z.*, 1929, **30**, 576.

using a *resonance method* (Fig. 106). The h.f. oscillator (G) is coupled to the untuned power circuit (I) by means of a variable inductor in order that the current flowing in circuit (I) may be varied. This current is measured by means of a thermo-element and galvanometer (II). High frequency oscillations are also induced in the resonance circuit (III) which contains the cell (C_1). The current in this circuit is measured by circuit (IV) which is carefully arranged so that the energy picked up from circuit (I) is a minimum.
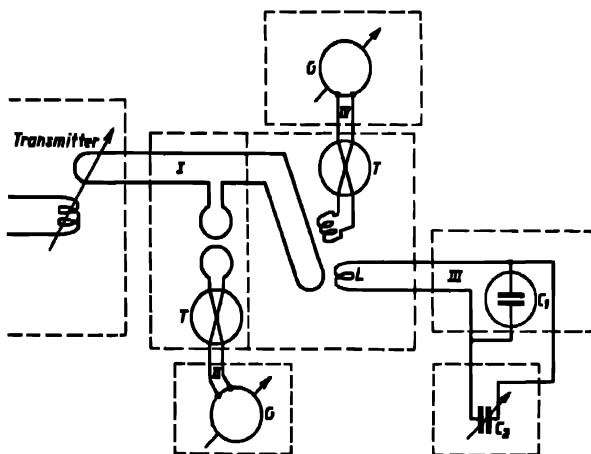
Fig. 106. SACK's method. Reproduced from H. FALKENHAGEN, *Electrolytes*, transl. by R. P. BELL (The Clarendon Press, Oxford, 1932)

At resonance the impedance of a circuit is equal to its resistance [*cf.* equation (12)]. The resistance of circuit (III) may be obtained from measurements of the resonance current. The resistance measured in this way is the equivalent resistance (R_s) in series with the capacitance of the circuit (acceptor circuit p. 524). It appears more correct to regard the electrolytic resistance (R_p) as being in parallel to the capacitance. It may thus be obtained from the relation,

$$R_s = \frac{R_p}{1 + \omega^2 C_p^2 R_p^2} \quad [cf. (16)];$$

or, as ω is large,

$$R_p = \frac{1}{\omega^2 C_p^2 R_s} . \tag{24}$$

The method was used to compare the conductance of solutions at high frequencies with that of a standard solution (KCl). WIEN [1] has adapted the barretter method (described above) for the measurement of conductance at high frequencies by replacing the spark gap with a high frequency electronic generator. Other methods have been described by DEUBNER [2] and MALSH [3].

(iii) *Transport Numbers in Electrolytic Solutions* (I - 8)

(a) *The Hittorf method* [4]

This method depends on the accurate determination of changes of concentration in the anolyte and the catholyte (*cf.* equation I - 72). In order that the changes of concentration set up during the electrolysis may not be obscured by mechanical or thermal mixing, it is necessary to reduce vibration and uneven heating of the cell to a minimum.

Fig. 107 illustrates a modern cell used by McINNES and DOLE [5]. The right angled bends were included to break up convection currents and led to a marked improvement in results. The anode was placed higher than the cathode to reduce gravitational mixing consequent on the decrease of concentration (and hence of density) of the anolyte.

The solution was carefully deoxygenated to ensure that no unwanted electrode process occurred. The current was measured using two coulometers in series with the cell, one on each side, so that leak currents might be detected. At the completion of the experiment the stop-cocks were closed and the solutions analysed by a differential electrometric titration capable of an accuracy of about 0·003%. A test of the
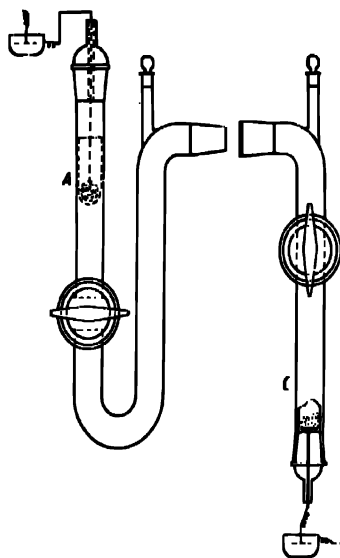
Fig. 107. Modern form of HITTORF cell. Reproduced from McINNES, *Principles of Electrochemistry* (Reinhold, New York, 1939)

[1] M. WIEN, *Ann. Physik*, 1931, 11, 429. See also O. NEESE, *ibid.*, 1931, 8, 929.

[2] A. DEUBNER, *Physikal. Z.*, 1929, 30, 049.

[3] J. MALSCH, *ibid.*, 1932, 12, 865.

[4] H. JAHN, *Z. Physikal. Chem.*, 1900, 33, 545.   E. W. WASHBURN, *J. Am. Chem. Soc.*, 1909, 31, 322.

[5] D. A. McINNES and M. DOLE, *J. Am. Chem. Soc.*, 1931, 53, 1357.

validity of each experiment is that no change in concentration occurs in the centre compartment. (*cf*. I - 8).

(b) *The moving boundary method* [1]

The condition for equality of the velocity of ions on either side of the boundary (*cf*. I - 8 Fig. 9), *i.e.* for the *boundary to remain sharp*, is

$$\frac{n_L}{c_L} = \frac{n_I'}{c_I} \quad \text{(KOHLRAUSCH regulating function [2]) *} \quad (25)$$

where n_L and c_L are the transport number and concentration of the ion being investigated (known as the *leading* ion) and n_I and c_I are the corresponding quantities for the indicator ion. In practice, the concentration of the indicator solution adjacent

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* If U_L and U_I are the mobilities of the leading and indicator ions, respectively, then the actual velocities of these ions will be

$$v_L = \frac{E_L}{d_L} U_L, \quad \text{and} \quad v_I = \frac{E_I}{d_I} \cdot U_I \quad (26)$$

where $\frac{E}{d}$ is the potential gradient in each homogeneous solution.

Now,

$$E = IR = I\left(\frac{d}{A\varkappa}\right),$$
$$= \frac{Id}{A} \cdot \frac{1}{c\,F\,(U + U')}; \quad (27)$$

where I is the current flowing through a cross-section of area A of the cell, $\varkappa$ is the specific conductivity and c the equivalent ionic concentration of the solution. U and U' are the ionic mobilities and d is the length of the column of solution. From (26) and (27)

$$v_L = \frac{U_L}{d_L} \cdot \frac{I\,d_L}{A} \cdot \frac{1}{c_L\,F\,(U_L + U_L')},$$
$$= \frac{I}{AF} \cdot \frac{n_L}{c_L}. \quad (28)$$

Similarly,

$$v_I = \frac{I}{AF} \cdot \frac{n_I}{c_I}. \quad (29)$$

For,

$$v_L = v_I,$$
$$\frac{n_L}{c_L} = \frac{n_I}{c_I}.$$

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[1] D. A. MACINNES and L. G. LONGSWORTH, *Chem. Rev.*, 1932, **11**, 171.

[2] F. KOHLRAUSCH, *Ann. Physik.*, 1898, **62**, 209. See also: L. G. LONGSWORTH, *J. Am. Chem. Soc.*, 1930, **52**, 1897.

to the boundary adjusts to the appropriate value during the electrolysis if the initial concentration is within certain limits of the required value (approximately 10 - 20%). The required concentration is calculated as accurately as possible using available data and equation (25); or is found experimentally by successive approximation.

The *formation of a sharp boundary* is best accomplished by means of an apparatus designed by MacInnes and Brighton[1] (Fig. 108). The two sections (A, D) of the tube joining the two electrodes are each fixed into a horizontal glass plate. (B, C). These plates are ground accurately plane and placed together. After the two sections of the cell have been filled respectively with the leading and indicator solutions the glass plates can be rotated so that the parts of the cell are joined together. The two solutions are sheared into contact forming a sharp horizontal boundary and the electrical circuit is thus completed. In a simpler apparatus used by Hartley and Donaldson[1] the boundary was formed in a capillary tube by removal of an *air bubble* separating the two solutions. The simplest method of boundary formation is by using indicator ions produced from an anode initially in contact with the leading solution (The *autogenic boundary*
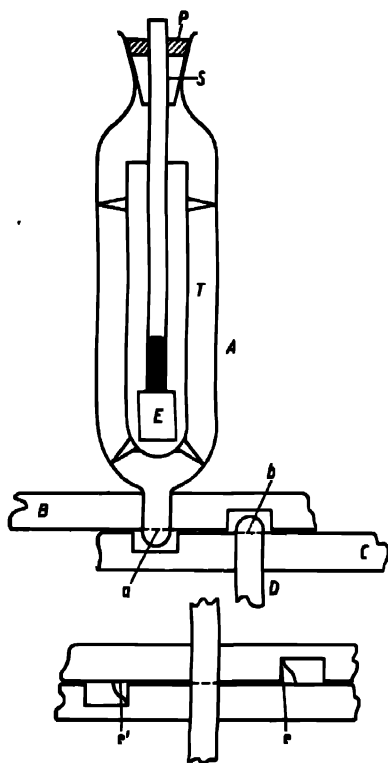
Fig. 108. Moving boundary cell. Reproduced from *Chem. Rev.*, 1932, **11**, 181
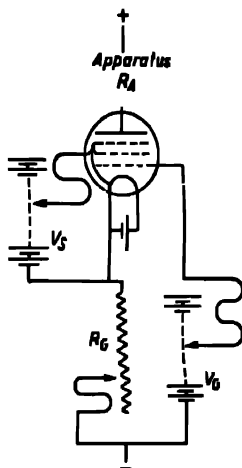
Fig. 109. Constant current device. Reproduced from *Trans. Faraday Soc.*, 1937, **33**, 400

[1] D. A. MacInnes and T. B. Brighton, *J. Am. Chem. Soc.*, 1925, **47**, 994.
[1] G. S. Hartley and G. W. Donaldson, *Trans. Faraday Soc.*, 1937, **33**, 457.

method) [1]. To ensure a uniform movement of the boundary, it is necessary that the production of the indicator ions should obey FARADAY's laws; this limits the use of the method to those metals which form suitable anodes, e.g. Cd.

The *direction of movement* of a boundary is always arranged so that the denser solution is below the less dense to reduce gravitational mixing. The boundary is conveniently *observed* by using a horizontal slit light source behind the graduated tube (see also Electrophoresis, p. 592).

A *constant current device* is generally employed. MacINNES *et al.* [2] used an elaborate mechanical regulator with a photo electric cell circuit actuated by a mirror galvanometer. HARTLEY and DONALDSON (*loc. cit.*) used a simpler, electronic, circuit (Fig. 109) which permitted a constancy of 1 part in 500 for currents of 0·5 to 4 mA. If the current tends to increase, the potential difference across R_G increases and the control grid of the pentode becomes more negative causing a decrease in the current. Conversely, if the current tends to decrease, the potential difference across R_G decreases, the control grid becomes more positive and the current increases.

One electrode compartment is completely enclosed and is filled with solution. The electrode is of a type at which no gas is produced during electrolysis, *e.g.* the silver-silver chloride electrode (*cf.* section 7, p. 582). In this way the movement of the boundary is measured with respect to the walls of the cell. However, the transport number is defined using the *velocity of the ions with respect to the solvent*. To obtain the movement of the boundary with respect to the solvent, *corrections* must be made for the *volume change* at the electrode and the transport of water across the boundary (these include the corrections for water transport analogous to those of the HITTORF method, Chap. I - 8). LEWIS [3] showed that a volume ΔV must be subtracted from the observed volume swept out by the boundary when one Faraday is passed through the cell. This is given by

$$\Delta V = V_{XB} - V_X - n_A \overline{V}_{AB} , \qquad (30)$$

where V_X, V_{XB} are the molal volumes of X, XB in the closed electrode $X \mid XB, B^- (e.g. \text{ Ag} \mid \text{AgCl, Cl})$; n_A is the transport number of the leading ion and $\overline{V}_{AB}$ is the partial molar volume of the leading electrolyte AB in the solution used.

[1] E. C. FRANKLIN and H. P. CADY, *J. Am. Chem. Soc.*, 1904, **26**, 499. D. J. LE ROY and A. R. GORDON, *J. Chem. Phys.*, 1938, **6**, 308, etc.

[2] D. A. MacINNES *et al.*, *J. Am. Chem. Soc.*, 1926, **48**, 1904.

[3] G. N. LEWIS, *ibid.*, 1910, **32**, 862.

According to LONGSWORTH [1] the results should also be corrected for the specific *conductance of the solvent,*

$$n_{corr.} = n_{obs.} \left(1 + \frac{\varkappa_{solvent}}{\varkappa_{solution}} \right) \tag{81}$$

(c) *The e.m.f. method*

The technique of preparing some reversible electrodes is described in section 7. Similar electrodes may be used in cells for the measurement of transport numbers (*cf.* Chapter VII).

(iv) *Ionic Migration in Gases* [2] (XII)

ZELENY [3] passed gas at a constant rate along a tube (TT') in which a pair of cylindrical electrodes CD and EF are situated (Fig. 110). The two centre electrodes CD and EF were separated
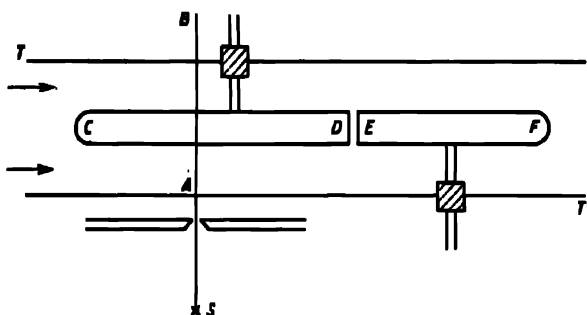
Fig. 110. Determination of mobilities of gaseous ions. Reproduced from H. A. WILSON, *Modern Physics* (Blackie, London, 1940)

by a narrow gap. Radiation from a radio-active substance S was limited to a narrow beam by the slit, and ionised the gas as it passed the plane AB. CD and EF were at zero potential and TT'

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[1] L. G. LONGSWORTH, *ibid.*, 1932, 54, 2741.

[2] J. J. THOMSON and G. P. THOMSON, *Conduction of Electricity in Gases*, Cambridge, 1928. K. K. DARROW, *Electrical Phenomena in Gases*, Williams and Wilkins, Baltimore, 1932. G. GLOCKLER and S. C. LIND, *Electrochemistry of Gases and other Dielectrics*, Wiley, New York, 1937. L. B. LOEB, *Fundamental Processes of Electrical Discharge in Gases*, Wiley, New York, 1939. J. D. COBINE, *Gaseous Conduction*, McGraw-Hill, New York, 1941. H. A. WILSON, *Modern Physics*, 2nd. Edition, Blackie, London, 1946.

[3] ZELÉNY, *Phil. Trans.* A., 1900, 195, 193.

was at a potential ψ. Ions formed in the plane AB were attracted to either TT' or CD, the actual path being the resultant of the motion due to this force and the motion of the gas stream. Ions reaching EF could be detected by means of a quadrant electro-meter (not shown) attached to it. The potential (ψ) was then adjusted until it was just great enough to prevent ions reaching EF, indicating that ions formed at the surface of the electrode TT' are just reaching the centre electrode at the gap between its two parts. If the radius of the outer electrode is b and that of the inner a, the mobility can be obtained from the expression

$$u = \frac{Q \ln b/a}{2 \pi \psi d} \, , \tag{35}$$

where Q is the volume of gas passing AB in unit time and d is the distance between the plane AB and the division in the centre electrode (cf. Chapter XII problem 3).

A *method* depending on the *reversal of the field* was first used by RUTHERFORD [1, 2]. The gas was placed between parallel plates a distance l apart. Ions of one sign only were produced at one plate; for example, by producing ions behind a hole in the plate which was covered with wire gauze and allowing the ions of one sign to pass through the gauze under a weak electric field. If another field F is maintained between the plates for a time t and then reversed, no ions will reach the other plate unless

t is greater than $\dfrac{l}{UF}$. The mobility may thus be determined by finding the value

of t for which the second plate just receives a charge. If the reversal is carried out many times, the charge on the second plate is built up to a value which can be more easily detected. If an alternating electric field $F = F_0 \sin \omega t$ [cf. equation (1)] is used the distance the ions move is given by

$$\int_0^{\frac{\pi}{\omega}} U F \, dt = \frac{2 u F_0}{\omega} \, , \tag{36}$$

and the critical condition is

$$l = \frac{2 U F_0}{\omega} \, . \tag{37}$$

Since both the above methods determine individual mobilities

[1] E. RUTHERFORD, *Proc. Camb. Phil. Soc.*, 1898, **9**, 401.

[2] See also P. LANGEVIN, *Ann. Chim. Phys.*, 1903, **28**, 289.

they are equivalent to both conductance and transport number measurements.

Gaseous conduction in flames[1] resembles conduction in solutions more closely than does that in cold gases, since, owing to the continuous rapid production of ions, a steady state is set up in which there is an appreciable concentration of ions. The conductance of a gas flame may be measured, if the flame issues from an insulating (quartz) burner, by inserting two platinum electrodes into the flame.

(v) *Ionic Migration in the Solid State* [2] (VI - 5)

The measurement of *conductance* of solids is often carried out by placing a single crystal, or a pellet of the pressed powder, between two metal electrodes. The resistance is then measured by an a.c. bridge method or by the d.c. method. The advantage of this method is that the temperature and atmosphere of the apparatus may be varied, and its main disadvantage is the uncertainty due to the contribution of contact resistance between the electrodes and the material. To reduce the latter the specimen is often platinised or graphitised at each end. In an alternative method due to GUDDEN *et al.* [3] the powdered material was mixed with a non-conducting dielectric such as oil and put between the plates of a condenser in an h.f. resonance circuit. Although this method is said to eliminate the effect of contact resistance, it is not capable of a high accuracy (usually about 10%).

Since the distinguishing feature of electrolytic conduction is the transport of matter, the *measurement of transport numbers* is an important experimental criterion of conduction mechanism [4]

[1] A. BECKER, *Wien-Harms Handbuch der Experimentalphysik*, 13, part. 1.   R. VICH-NIEVSKY, *Trans. Faraday Soc.*, 1940, 42, 322. H. A. WILSON, *Modern Physics*, 2nd. Edition Chap. XV., Blackie, London, 1940.

[2] E. FRIEDRICH and W. MAYER, Z. *Elektrochem.*, 1026, 32, 566. E. PODZUS, *ibid.*, 1933, 39, 75. W. SEITH, *ibid.*, 1936, 42, 085. R. M. FUOSS, *J. Am. Chem. Soc.* 1937, 59, 1703. W. MAYER, Z. *Elektrochem.*, 1944, 50, 274. M. FOEX, *Compt. rend.*, 1945, 220, 859.

[3] B. GUDDEN, *Ann. Physik*, 1932, 14, 193.

[4] G. v. HEVESY, *Geiger-Scheel Handbuch der Physik*, 13, Chap. 7.

(But see however WAGNER [1] on Ag_2S). The *general procedure* followed by TUBANDT *et al.* [2] for determining the transport number of a substance AX was to place three discs of AX and three discs of AY (known to be a pure cationic conductor) between two electrodes of A (Fig. 111). The weights of the discs and the electrodes were accurately known and a known quantity of current was passed through the cell. When electroly-
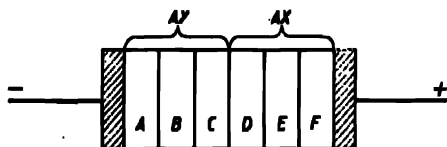
Fig. 111. Transport numbers in solids

sis occurred, the discs adjacent to the electrodes stuck to them and were weighed with them to determine the loss of material from the anode and the gain at the cathode, from which the transport number can be calculated. The conductor AY was used to check the actual current passing through the cell (the current measured outside the cell might include leak currents which occur readily in such highly resistant systems) and to ensure that negative ions remain near the anode (otherwise the cathode deposit is very irregular, protuberances known as "trees" being formed). An additional check on the experiment is made by weighing the discs B and E which should not alter in weight (*cf.* HITTORF method for solutions, I - 8).

7. Reversible Electromotive Force (VII, VIII)

(i) *The Measurement of Potential* [3]

The usual laboratory *standard of potential difference* is the WESTON cell,

$$Hg \mid Hg_2SO_4 \text{ (sat.) } CdSO_4 \text{ (sat.) } \mid Cd \text{ (Hg) ;}$$

which is generally set up in a sealed glass H-tube. Both acid and neutral electrolytes are employed, the one having no great advan-

[1] C. WAGNER, *Z. Physikal. Chem. B.*, 1933, **21**, 42; **23**, 469.

[2] C. TUBANDT, *Wien-Harms Handbuch der Experimentalphysik*, **12**, part. III.

[3] P. VIGOREUX and C. E. WEBB, *Electrical and Magnetic Measurements*, Chap. II, Blackie, London, 1941.

tage over the other. The most important condition of use is that only very small currents (of the order 10^{-6} amps) should be taken from the cell. A cell which has been short circuited for more than a second may take many days to return to its original e.m.f. This is due to polarisation of the electrodes, with possibly the formation of an oxide film on the anode (*cf.* ROTHSCHILD [1]).

(a) *The potentiometer*

The simple slide wire method is unsuitable for accurate work since the slide wire would be inconveniently long. In the *modern type of potentiometer* [2] most of the slide wire is replaced by resistance coils.
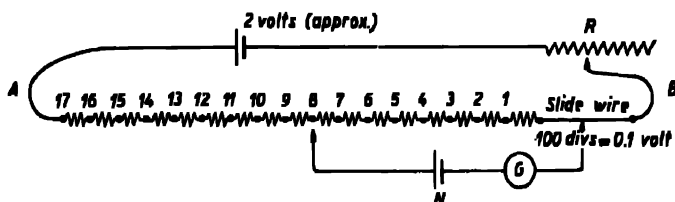
Fig. 112. Simple potentiometer

In the potentiometer shown in Fig. 112 the slide wire consists of 17 resistance coils and a small rotary resistance, all having the same resistance. The potential can thus be adjusted in steps of 0·1 v. with the selector knob and to the nearest millivolt with the rotary resistance, which has a calibrated dial. The potentiometer is first adjusted, so that a potential drop of exactly 1·8 v. exists from A to B, by means of a standard cell (N). To do this, the dials of the potentiometer are set to the e.m.f. of the standard cell and the resistance (R) is adjusted until no deflection of the galvanometer is obtained. The standard cell (N) is then replaced by the unknown e.m.f., and the potentiometer balanced again, when the e.m.f. of the unknown may be read directly from the setting of the dials. Potentiometers working on this principle are available for the measurement of potential differences from 10^{-6} v. to 2 v.

Higher potentials may be measured by connecting standard cells in opposition to the e.m.f. to be measured, or, less satisfactorily, by the use of a potential *divider*. In the latter a high resistance is connected across the points between which the e.m.f. is to be measured and the e.m.f. across a known fraction of this resistance is measured with the potentiometer as described above. The e.m.f. across the ends of the resistance can then be calculated.

(b) *The valve potentiometer*

For work in which the e.m.f. to be measured is associated with

[1] Lord ROTHSCHILD, *Proc. Roy. Soc.* B., 1938, **125**, 283.

[2] Ref. 3 p. 578, Chap. V.

a very *high internal resistance* (*e.g.* the glass electrode) valve potentiometers [1] are used, since these require very small currents for operation. Such potentiometers are also useful for systems in which the equilibrium would be disturbed by the current drawn by the potentiometer described above when it is slightly off balance.
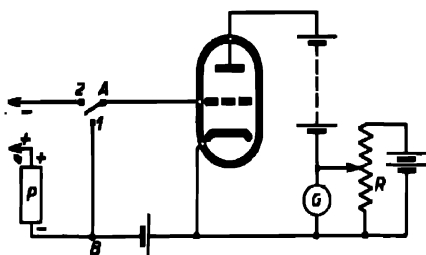
Fig. 113. Valve potentiometer

The *basic circuit* of a valve potentiometer is shown in Fig. 113. Essentially the unknown e.m.f. (X) is compared with a known e.m.f. (P) in a high resistance circuit (the grid circuit of a valve). The small deviations from balance are amplified by means of a valve and indicated on a sensitive galvanometer. The instrument is *standardised* by connecting together the points (A) and (B) in the grid circuit by putting the switch at (A) in position (1), and then adjusting the resistance (R) until no current flows through the galvanometer (G). For *measuring an unknown e.m.f.* (X) the switch (A) is put in position (2) so that (X) is introduced into the grid circuit together with a potentiometer (P) (similar to that described above) so that the e.m.f.'s of (X) and (P) are acting in opposition. The potentiometer (P) is adjusted until again no current flows through the galvanometer (G). The potential of the point (A) must then be equal to that of (B), and the e.m.f. of the potentiometer (P) is equal and opposite to that of the unknown (X). The unknown e.m.f. may thus be read directly on the dials of the potentiometer.

Any current drawn from the unknown must pass round the grid circuit of the valve, hence the current required for operation is controlled principally by the impedance between the grid and the cathode. In an ordinary valve this current is of the order of 10^{-10} amp., if the grid is kept negative with respect to the cathode. This current may be reduced to about 10^{-17} amp. by using a valve of special construction called an *electrometer valve*. In this type of valve special care is taken to insulate the grid from the cathode, and to remove traces of gas from the envelope in order to reduce conduction between the grid and cathode.

[1] K. H. GOODE, *J. Am. Chem. Soc.*, 1922, 44, 26; 1925, 47, 2483. R. L. GARMAN and M. E. DROSZ, *Ind. Eng. Chem.* (*Anal. Ed.*), 1939, 11, 398. M. DOLE, *The Glass Electrode*, Chapman and Hall, London, 1941. E. MOUTON, *Trans. Faraday Soc.*, 1928, 24, 5; 1948, 44, 588, *J. Sci. Inst.*, 1932, 9, 289. H. T. S. BRITTON, *ibid.*, 1946, 23, 89.

(ii) *Reversible Electrodes*

According to LUTHER, GERKE and BOCKRIS *et al.* the following observations [1] indicate that the *electrode is not behaving reversibly*,

1. Fluctuations occur in the e.m.f.
2. Two apparently identical electrodes in the same solution give a different e.m.f.
3. Changes occur in the e.m.f. if the electrode is shaken.
4. Changes in the concentration of the solution do not result in changes in the e.m.f. which agree with those predicted by the NERNST equation.
5. The potential does not rapidly return to the equilibrium value after polarisation.

Standard Half Cells

Hydrogen electrodes are best prepared [2] by electrolysing a pure solution of platinic chloride containing 1% of platinum * between two platinum foil electrodes. A suitable current is obtainable directly from a 2 v accumulator and its direction is reversed every two or three minutes. The electrolysis is continued until a velvety black deposit is obtained (usually 2 - 4 hours). The electrodes are then carefully washed in conductivity water. If such electrodes are used in carefully purified solutions they will reach equilibrium in 15 minutes; an electrode which does not reach equilibrium within 30 minutes is usually poisoned. It appears unnecessary to keep part of the electrode above the level of the solution, although this is often done. (The depth of the bubbler, however, has an effect of the order 3 μv./cm. [3] owing to the supersaturation of the solution with hydrogen at a higher hydrostatic pressure). Once an electrode has reached equilibrium it will maintain the reversible hydrogen potential for several days without hydrogen bubbling [2], if the solution is saturated with hydrogen and it is in a hydrogen atmosphere, although in normal use hydrogen is kept bubbling continuously. When not in use, hydrogen electrodes should be kept in conductivity water as they lose their catalytic properties if allowed to become dry. Several types of electrode vessel have been described [4]. Hydrogen

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* In contrast to the preparation of electrodes for conductivity cells, the use of addition agents such as lead acetate or formic acid, although they produce a thick deposit rapidly, is not advisable since the resulting electrodes have a much shorter life.

[1] R. LUTHER, *Z. Elektrochem.*, 1907, **13**, 289. R. H. GERKE, *Chem. Rev.*, 1925, **1**, 377. J. O'M BOCKRIS, J. F. HERRINGSHAW *et al.*, *Faraday Soc. Discussion*, 1947, **1**, 328.

[2] J. H. ELLIS, *J. Am. Chem. Soc.*, 1916, **38**, 737.

[3] G. I. HILLS and D. I. G. IVES, *Nature*, 1949, **163**, 997.

[4] J. HILDEBRAND, *J. Am. Chem. Soc.*, 1913, **35**, 847. C. H. BAILEY, *ibid.*, 1920, **42**, 45. A. J. LINDSEY, *Analyst*, 1932, **57**, 573.

gas should be deoxygenated by passing through alkaline pyrogallol[1] or over palladised asbestos at about 350 °C.

For *calomel electrodes* redistilled mercury should be used, since traces of foreign metals[2] have a marked effect on the potential. A.R. quality mercurous chloride is usually suitable for most purposes if ground in a mortar with a little mercury and KCl solution to reduce traces of mercuric chloride. For accurate work (better than ±0·001 v.) very pure samples of Hg_2Cl_2 may be prepared electrolytically[3]. Correspondingly recrystallised A.R. KCl may be used in conductivity water for most purposes, but for accurate work pure KCl may be prepared by two precipitations with pure HCl gas followed by fusion of the air dried product[4].

Silver-Silver Chloride electrodes are usually supported on platinum wire. Several methods have been proposed for their preparation: (a) the thermal decomposition of a paste of Ag_2O and $AgClO_3$ held on the platinum wire; (b) the electrolytic deposition of Ag from a cyanide solution followed by anodic electrolysis in dilute HCl (10 - 20 mA for 1 - 2 hours[5]); (c) thermal decomposition of an Ag_2O paste (350 - 450 °C) and covering with AgCl paste prepared by evaporating ammoniacal AgCl solution over concentrated H_2SO_4[6]; (d) thermal decomposition of an Ag_2O paste followed by anodic electrolysis in an HCl solution[7]. There is some evidence that the last method is the most satisfactory[8].

(iii) *Electro-analytical Methods* (VI - 3, VIII - 3)

The ordinary methods of conductometric and potentiometric analysis[9] described in chapters VI and VIII may have to be refined for special purposes. For example, very high accuracy (0·003%) in potentiometric titrations may be attained by using a differential method and weight burettes[5 p. 371]; and for the titration of certain organic redox systems exclusion of oxygen is necessary[10].

(a) *Gravimetric electrolytic analysis*

Electrolytic deposition provides a very convenient method for

[1] J. S. HALDANE and R. H. MAKGILL, *Analyst*, 1933, **58**, 378.

[2] G. A. HULETT and H. D. MINCHIN, *Phys. Rev.*, 1905, 21, 388; 1911, 33, 307.

[3] G. A. HULETT, *Phys. Rev.*, 1906, 22, 334. J. H. ELLIS, *J. Am. Chem. Soc.* 1916, **38**, 740. G. F. LIPSCOMB and G. A. HULETT, *ibid.*, 1916, **38**, 21.

[4] G. D. PINCHING and A. G. BATES, *J. Res. Nat. Bur. Stand.*, 1946, **37**, 311.

[5] A. A. NOYES and J. H. ELLIS, *J. Am. Chem. Soc.*, 1917, **39**, 2532.

[6] E. GUNTELBURG, *Z. physikal. Chem.*, 1926, **123**, 199.

[7] H. S. HARNED, *J. Am. Chem. Soc.*, 1929, 51, 416.

[8] P. T. GILBERT, *Faraday Soc. Discussion*, 1947, 1, 320.

[9] I. M. KOLTHOFF and H. A. LAITINEN, *pH and Electro Titrations*, J. Wiley, New York, 1941.

[10] H. E. CAMERON, *J. Phys. Chem.*, 1938, **42**, 1217. L. MICHAELIS in A. WEISS-BERGER, *Physical Methods of Org. Chem.*, Interscience, New York, 1946.

the gravimetric analysis of metals since, by using controlled conditions (both chemical and electrical), the constituent metals may be completely separated from a solution containing several metal salts. The potential of the cathode with respect to a reference electrode is usually controlled throughout the deposition by varying the current in order to maintain the appropriate conditions for deposition of the required ion These conditions may be predicted very roughly if the reversible potential and overpotential of the particular ion are known (cf. Chapter XI) but the conditions used in practice are usually empirical. A detailed description of many of these electrolytic separations is given by SAND[1].

(b) *Controlled potential analysis*

In analytical (and also preparative) electrolysis the controlling factor is the electrode potential[2]. An apparatus for controlling an electrode potential throughout an electrolysis was originated by HICK-LING (who coined for it the name *potentiostat*) and by CALDWELL, PARKER and DIEHL[3]. An improved apparatus due to LIN-GANE[4], however, permits more complete control of the electrode potential (Fig. 114). The current passing through the cell
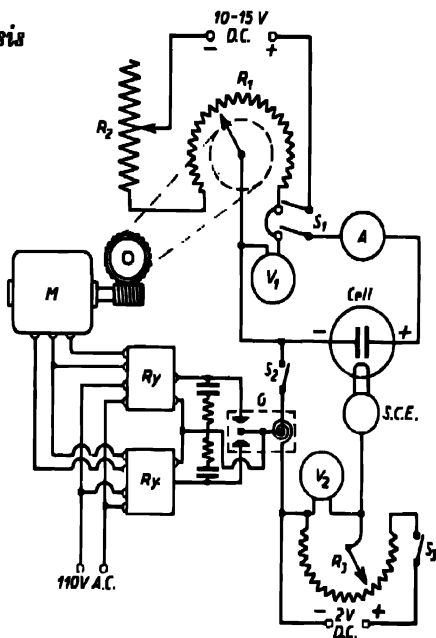
Fig. 114. Potentiostat. Reproduced from *Faraday Soc. Discussion*, 1947, 1, 205

[1] H. T. S. SAND, *Electrochemistry and Electrochemical Analysis*, Blackie, London, 1940.

[2] W. BÖTTGER, *Physikalische Methoden der Analytischen Chemie*, Teil II, Leipzig, 1936.

[3] A. MacKLING, *Trans. Faraday Soc.*, 1942, 38, 27; C. W. CALDWELL, R. C. PARKER and H. DIEHL, *Ind. Eng. Chem. (Anal. Ed.)*, 1944, 16, 532.

[4] J. J. LINGANE, *Ind. Eng. Chem. (Anal. Ed.)*, 1945, 17, 332.

is controlled by the rheostat (R_1), driven by an electric motor. This motor is actuated by a galvanometer relay (G), via electronic relays (R_y). The galvanometer relay operates when the potential difference between the working and reference electrodes differs from the opposing e.m.f. set on the rheostat (R_2). The current through the cell is then altered automatically to return the electrode potential to the required value.

Several applications of the potentiostat are reviewed by LINGANE [1].

(c) *Polarography* (XI - I) [2]

For much routine work the electrodeposition of metals has been replaced by *polarographic analysis* which has the advantage of speed and also requires very small quantities of solution. The *essentials of the apparatus* are illustrated in Fig. 66 p. 409. In practice the instrument is made to function as nearly as possible automatically (Fig. 115). The resistance wire is wound on a drum (B) which is geared to another drum (C) carrying a photographic recording paper. Thus, when the potentiometer drum is driven at a low speed by a motor (A), the record-

Fig. 115. HEYROVSKY—SHIKATA polarograph. Reproduced from I. M. KOLTHOFF and J. J. LINGANE, *Polarography* (Interscience, New York, 1941)

[1] J. J. LINGANE, *Faraday Soc. Discussion*, 1947, 1, 203.
[2] J. J. LINGANE and I. M. KOLTHOFF, *Chem. Rev.*, 1039, 24, 1. I. M. KOLTHOFF and J. J. LINGANE, *Polarography*, Interscience, New York, 1941. J. HEYROVSKY, *Polarographie*, Springer, Leipzig, 1941. J. HEYROVSKY, *Metallwirt*, 1944, 23, 333.

ing drum rotates in proportion to the applied potential and the
current is recorded by the action of the light beam from a mirror
galvanometer (E). The current potential curve thus produced
is known as a polarogram.

The periodic change in current due to the growth of the drop
is reduced by use of a galvanometer of long period but may be
almost eliminated by the connection of a large condenser (about
2000 μF.[1]) in parallel with the galvanometer shunt. This is
because the rapid small variations in current will be absorbed in
charging and discharging the condenser and will thus not reach the
galvanometer.

Cathode-ray tubes have been used as indicators[2] and MATHE-
SON and NICHOLS[3] obtained a complete polarogram on an oscillo-
graph screen, using a rapid drop rate synchronised with the time
base of the oscil-
lograph. However,
only recently has
RANDLES[4] shown
how a direct reading
cathode-ray polaro-
graph (Fig. 116) can
be used with analytic-
al accuracy compa-
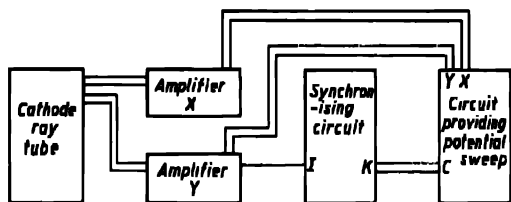
Fig. 116.
Block diagram of cathode-ray polarograph [4]

rable to that of the HEYROVSKY polarograph. A polarogram
is obtained for each drop by increasing the potential across
the cell at a constant rate during the existence of the drop.
This increase of potential is provided by charging up a con-
denser through a resistance; to obtain a stationary figure on
the oscillograph, this is repeated for each drop. The condenser
is short-circuited as each drop falls, and charging recom-
menced after a predetermined time has elapsed, by means
of a relay (compare the time base p. 536) actuated by a
circuit which receives an impulse as the drop falls, due to

[1] J. J. LINGANE and II. KERLINGER, *Ind. Eng. Chem.* (*Anal. Ed.*)., 1940, 12, 757.
[2] R. H. MULLER, *et al.*, *Ind. Eng. Chem.* (*Anal. Ed.*), 1938, 10, 339. J. BOEKE
and H. VAN SUCHTELEN, *Philips Tech. Rev.*, 1939, 4, 213.
[3] L. A. MATHESON and N. NICHOLS, *Trans. Am. Electrochem. Soc.*, 1938, 73, 193.
[4] J. E. B. RANDLES, *Trans. Faraday Soc.*, 1948, 44, 322.

the sudden change of the current in the cell. An electronic device is also employed to maintain the rate of change of the potential difference across the cell constant, and independent of the magnitude of the current flowing through the cell. The potential difference across the cell is amplified by means of a direct coupled amplifier (X) and applied to the X plates of an oscillograph. The current is measured by similarly amplifying the potential difference across a resistance in series with the cell and applying it to the Y plates. A current voltage curve is thus obtained on the oscillograph screen.

Capillaries for the dropping electrode may be either drawn from larger capillary tubing or very fine capillaries such as 0·03 mm. bore thermometer tubing may be used. The capillary is often connected to the mercury reservoir by means of carefully cleaned rubber pressure tubing. Since the contact of mercury with rubber is undesirable because of the introduction of traces of capillary active substances, some workers [1] have used an all-glass connection. For general purposes, however, the use of a connecting tube of a polyethylene plastic appears quite satisfactory.

It is necessary to use *mercury* of a high degree of purity, which may be obtained by the use, first, of one of the usual "wet" methods, the best of which appears to be that of v. NARAY-SZABO [2] followed by distillation in a stream of air [2 p. 669].

The electrolytic cell used has a form depending on the particular purpose for which it is required. In the simplest, the mercury pool at the bottom (which is virtually non-polarisable with the small currents passed) is used both as an anode and as a reference electrode, but external anodes and reference electrodes are used in more accurate work (*cf.* the capillary electrometer).

At *anodic potentials* the mercury electrode becomes unusable in many solutions because of the dissolution of the mercury [3]. Under these conditions similar types of current-voltage curves, which may be used for analytical purposes, are obtained using *platinum micro electrodes* which may be stationary, rotating[4], or vibrating[5].

[1] *e.g.* J. J. LINGANE and I. M. KOLTHOFF, *J. Am. Chem. Soc.*, 1939, **61**, 825.

[2] S. v. NARAY-SZÁBÓ, *Z. Electrochem.*, 1925, **31**, 95.

[3] I. M. KOLTHOFF and C. S. MILLER, *J. Am. Chem. Soc.*, 1941, **63**, 1405. W. MacNEVIN and E. W. BALIS, *ibid.*, 1943, **65**, 660. J. O'M. BOCKRIS and R. PARSONS, *Coll. Czech. Chem. Comm.*, 1947, **12**, 833; *Nature*, 1947, **160**, 282.

[4] H. A. LAITINEN and I. M. KOLTHOFF, *J. Phys. Chem.*, 1941, **45**, 1079. D. THURLEY, M.Sc. *Thesis*, London, 1947.

[5] E. D. HARRIS and A. J. LINDSAY, *Nature*, 1948, **162**, 413.

8. The Electrical Double Layer (X)

(i) *Electrocapillarity and the Capacity of the Double Layer* (X - 1)

(a) *The capillary electrometer*

An important method of studying the structure of the double layer is the measurement of the re-lation between interfacial tension and potential. The *classical work* of GOUY[1] was carried out using a capil-lary electrometer which differed little from that originated by LIPPMANN (see Fig. 49). Recently *improvements* have been made in the experimental technique by KOENIG, CRAXFORD[2] and HANSEN and WILLIAMS[3].

A typical apparatus is shown in Fig. 117. Although it has been stated[4] that oxygen has no effect on the electrocapillary curve obtained using an electrometer (for example, GOUY used solutions in open beakers), most modern workers prefer to use de-oxygenated solutions. It is very im-portant that no traces of capillary-active substances are present in the

Fig. 117. Capillary electrometer

solution. The solution is prepared in a hydrogen atmosphere and then passed into the cell through C. The electrode (B) may act as anode and reference electrode because very small currents are passed through the cell, and since the area of the electrode (B) is very much larger than that of the mercury in the capillary, the former is unlikely to be polarised. However, the ohmic drop

[1] G. GOUY, *Ann. Chim. Phys.*, 1903, 29, (VII), 145. *Ann. Physique*, 1917, 7, 129, *etc.*

[2] F. O. KOENIG, *Z. physikal. Chem.*, A, 1931, 154, 454. S. R. CRAXFORD, *Disser-tation*, Oxford, 1936.

[3] L. A. HANSEN and J. W. WILLIAMS, *J. Phys. Chem.*, 1935, 39, 439.

[4] D. C. GRAHAME, *J. Am. Chem. Soc.*, 1941, 63, 1207.

(usually small) in the solution is included in the measured e.m.f. so that it appears preferable to have separate electrodes to perform the functions of anode and reference electrode.

The *capillary* can be made from thermometer tubing and drawn out to about 10^{-3} cm. internal diameter. The sensitivity is greater the less the shape of the tube differs from cylindrical, but it must not be exactly cylindrical otherwise the position of the meniscus becomes indeterminate. The measurement of interfacial tension is then made by adjusting the height of the mercury column (D) by means of nitrogen from a cylinder, so that the lower meniscus is at a constant level. The height is measured using a travelling microscope. For accurate work it is important that the *temperature* of the mercury column should be constant since the density of mercury changes considerably with temperature, and it is preferable that the whole apparatus be in a thermostat.

(b) *The use of the dropping mercury electrode*

Electrocapillary curves have also been obtained by calculating the interfacial tension from the weight of the drop of mercury falling from a capillary tube [1]. This method appears to be more satisfactory than the electrometer method for non-aqueous solutions since the liquid no longer wets the glass perfectly, and the angle of contact between the mercury and the glass is less than 180° by an uncertain and variable amount. Oxygen in the solution appears to affect the results obtained by this method [2].

For *solid metals* FRUMKIN [3] has shown that approximate electrocapillary curves may be obtained by measuring the contact angle between a gas bubble and the metal surface.

Values of the *charge on the electrode surface* and *capacity* of the double layer can be obtained from electrocapillary curves by graphical differentiation (*cf.* equation X - 8) but the method is somewhat inaccurate and more satisfactory values are obtained by direct measurement. PHILPOT [4] has measured the current required to keep an expanding mercury surface (dropping electrode)

[1] S. R. CRAXFORD and H. A. C. McKAY, *J. Phys. Chem.*, 1935, **39**, 545.

[2] J. HEYROVSKY and R. SIMUNEK, *Phil. Mag.*, 1929, 7, (7), 951.

[3] A. N. FRUMKIN, *Act. Sci. Ind.* (Paris) No. 373; *Physikal. Z., U.R.S.S.*, 1933, **4**, 239.

[4] J. St. L. PHILPOT, *Phil. Mag.*, 1932, 13, (7), 775.

at constant potential, from which the charge density in the double layer is obtained from equation X - 9 (*cf.* problem X - 8). Correction can be made for any *"faradaic" current* which does flow, but it is preferable to reduce this by very careful purification of the solution in the absence of oxygen, and especially by use of *electrolytic purification* (Section 8).

(c) *Electrode capacity by direct measurement*

(1) A. C. m e t h o d s

The capacity of the electrode double layer may be obtained more accurately by direct measurement. Many authors[1,2] have included the cell in an *a.c. bridge* (*cf.* sections 4 and 6). By using
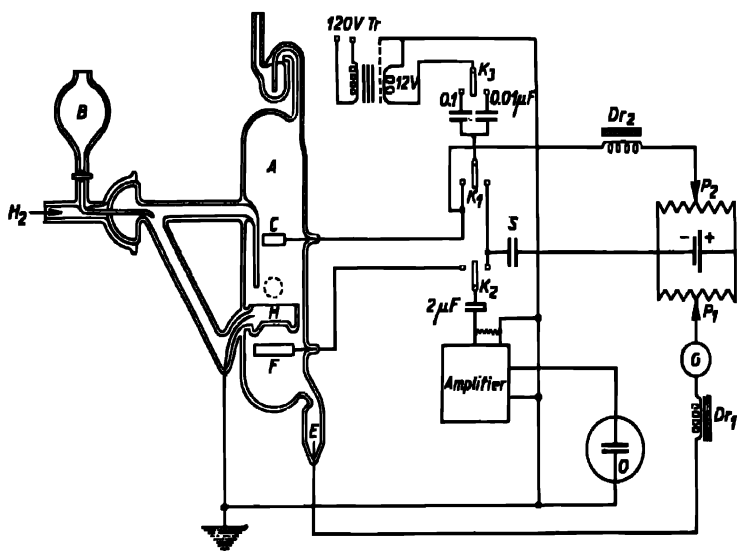
Fig. 118. A.C. method for the determination of the capacity of a mercury electrode. Reproduced from *Acta Physicochim. U.R.S.S.*, 1936, 4, 820

an auxiliary electrode of very much larger capacity than the test electrode (*e.g.* by having the former of much larger area than the

[1] M. WIEN, *Ann. Physik*, 1902, **8**, 373. F. KRUGER, *Z. physik. Chem.*, 1908, 45, 1. I. WOLFF, *Phys. Rev.*, 1926, 23, 755. G. JONES and S. M. CHRISTIAN, *J. Am. Chem. Soc.*, 1935, 57, 272.

[2] P. DOLIN and B. ERSHLER, *Acta Physicochim., U.R.S.S.*, 1940, 13, 747. D. C. GRAHAME, *J. Am. Chem. Soc.*, 1946, 68, 301.

latter), the measured capacity may be ascribed entirely to the test electrode (cf. equations 8, 10). The alternating potential across the electrode is kept below 15 mv. [1, 10] since the smaller the potential amplitude the closer the measured capacity approaches the true differential capacity $\left(\dfrac{\partial \sigma}{\partial \psi}\right)$ at a given potential.

If the current leak through the electrode is very small, i.e. the electrode impedance is almost entirely capacitative, the electrode capacity may be measured by passing a known a.c. through the cell and observing the potential difference across it. This method was used by BORRISOVA and PROSKURNIN [1] for mercury electrodes, which fulfil this condition closely until hydrogen evolution becomes significant.

The apparatus is shown in Fig. 118. A 50 c.p.s. a.c. (Tr) is passed through a circuit containing the cell (A) (or standard condensers) and a condenser, having an impedance much larger than the cell, which serves as a constant current device. The amplitude of the potential across the cell is compared with that across the standard condenser by amplifying and observing it with a cathode-ray oscillograph.

(2) D. C. transient methods

The electrode capacity can also be measured by observing the rate of change of the potential when the electrode is charged with direct current. In early work the rapid potential changes were observed using mechanical oscillographs [2]. *Charging curves at high current densities* have more recently been carried out using a cathode ray oscillograph as an indicating instrument [3].

At *low current densities* the experimental conditions become more important, since the depolarising impurities present must be reduced to such concentrations that the current due to their

[1] T. I. BORRISOVA and M. A. PROSKURNIN, *Acta Physicochim.*, *U.R.S.S.*, 1936, 4, 819.

[2] F. R. BOWDEN and E. K. RIDEAL, *Proc. Roy. Soc.* A., 1928, 120, 53. E. BAARS, *Sitzungsber. Ges. Förd. Naturwiss. Marburg*, 1928, 63, 213.

[3] I. M. BARCLAY and J. A. V. BUTLER, *Trans. Faraday Soc.*, 1940, 36, 128. A. HICKLING, *ibid.*, 1940, 36, 364.

reduction is negligible in comparison with the charging current. Such conditions may be obtained fairly readily for platinised platinum electrodes [1] and the potential change is sufficiently slow to be measured with an ordinary potentiometer. For a smooth platinum electrode a special technique was developed by ERSHLER [2] who used an apparatus in which an extremely small volume of catholyte (5 - 6 mm.[3]) was used so that the depolariser present could be readily removed by polarisation. BOWDEN and GREW [3] measured cathodic charging curves at a mercury electrode at very low current densities, by preparing the solution in a high vacuum system and then sealing the catholyte with the electrode entirely into glass. The electrode was then polarised through a bulb of conductivity glass and another similar bulb was used for the connection to the reference electrode.

The principal advantage of the a.c. methods and the d.c. charging method is that unlike electrocapillary methods they can be used for solid, as well as liquid, metals [4]. However, purification of the solution must be extremely rigorous (cf. section 9).

(ii) *Electrokinetic Measurements* (X - 8)

(a) *Electrophoresis*

The recent extensive development in the technique of electrophoresis measurements is largely due to their *biochemical applications*. Two principal types of apparatus, the macroscopic and the microscopic, are used.

(1) T h e   m a c r o s c o p i c   m e t h o d

This is essentially a development [5] of the moving boundary method which has been described for the determination of transport numbers. The type of apparatus used by TISELIUS has been illustrated (Chap. X, Fig. 58) and described in Chapter X.

[1] A. N. FRUMKIN and A. SLYGIN, *Acta Physicochim.*, *U.R.S.S.*, 1935, 3, 711; 1936, 4, 911; 1936, 5, 819.

[2] B. ERSHLER, *ibid.*, 1937, 7, 827.

[3] F. P. BOWDEN and K. E. W. GREW, *Faraday Soc. Discussion*, 1947, 1, 86.

[4] B. ERSHLER, *ibid.*, 269.

[5] L. G. LONGSWORTH, *Chem. Rev.*, 1942, 30, 323.

Since both the liquids used in these experiments are colourless special methods have been developed for following the movement of the boundary. SVEDBERG used the fluorescence of protein solutions produced by ultra violet light to make the boundary visible, but the more common *"schlieren" method* is based on the difference of refractive index of the two liquids [1].

The principle of the schlieren method is illustrated in Fig. 119. The image of a brilliantly illuminated slit (S) is formed by the lens (L) at (M). The electrophoresis tube (T) is placed immediately behind the lens (L), and an image of the tube is formed on the screen (R) by the camera lens (C). If the material in the electrophoresis tube contains a refractive index gradient (*e.g.* at a boundary), the light passing through this is deflected downwards
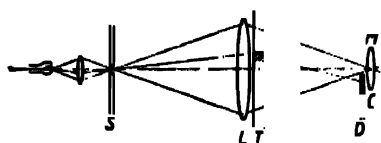
Fig. 119. Schlieren method

from its normal path. This deflected ray may be intercepted by a straight edged opaque plate (D) placed immediately in front of the camera lens (C) without intercepting the undeflected rays. Thus a region with a refractive index gradient appears on the screen (R) as a dark band.

Further developments of this technique by PHILPOT, SVENSSON and LONGSWORTH [1] using a diagonal slit with a cylindrical lens, and a mechanical "scanner" respectively have enabled a direct photographic record to be made of the electrophoretic pattern. The latter is a plot of the refractive index gradient in a thin layer of solution against the thickness of the layer and allows an estimate of the concentrations of the various components to be made during an electrophoretic separation of a mixture.

(2) The microscopic method

In the micromethod the motion of individual particles is observed either microscopically or ultra microscopically. The theoretical treatment of cylindrical cells is simpler than that of rectangular cells. The former were used by MATTSON [3]. HENRY [4],

[1] A. TISELIUS, *Trans. Faraday Soc.*, 1937, **33**, 524.

[2] J. S. L. PHILPOT, *Nature*, 1938, **141**, 283. H. SVENSSON, *Kolloid-Z.*, 1939, **87**, 181. L. G. LONGSWORTH, *J. Am. Chem. Soc.*, 1939, **61**, 529.

[3] S. MATTSON, *J. Phys. Chem.*, 1928, **32**, 1532; 1933, **37**, 223.

[4] D. C. HENRY, *J. Chem. Soc.*, 1938, 997.

however, has pointed out that, among other objections, the
difficulty of observing the flow exactly at the plane of zero electro-
osmotic flow (see Chap. X) makes
measurements in this type of
cell difficult to interpret. The
theory of the rectangular cell is
much simplified if the ratio of
width to depth is greater than
20 : 1. The planes of zero electro-
osmotic flow are at 21·1% of the
thickness from the top and bot-
tom of the cell. A *typical modern
cell*[1] is shown in Fig. 120.
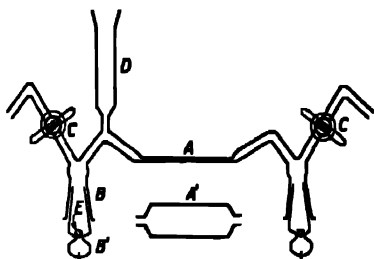
Fig. 120. Micro electrophoresis cell.
Reproduced from *Ind. Eng. Chem.*,
1940, 12, 703

The observation cell (A) was constructed of two polished Pyrex glass slides
25 × 75 × 1 mm. about 1 mm. apart, "laced" along the side with Pyrex rod and
sealed to the tubes carrying the joints into which the electrodes (B′) are inserted.
This cell appears to function satisfactorily without grease on taps and joints, and
since it is of all glass construction, it may be used for non-aqueous solutions.

(b) *Electro-endosmosis*

Two principal techniques have been used for the study of
electro-endosmosis. In one the solid material is in the form of a
porous plug which functions as a large number of capillaries. The
dimensions of these capillaries cannot be measured directly but
may be estimated by measuring the conductance of the plug
when filled with a solution of known conductance. This procedure
is however uncertain because of the unknown contribution of the
surface conductance. A typical example of this method is the work
of HAM and HODGSON who modified the apparatus of FAIR-
BROTHER and MASTIN[2] for the measurement of electro-osmosis
at carborundum powder. A circulating system was used, the rate
of flow through the carborundum plug being indicated by the
movement of a bubble in the capillary joining the two electrode
compartments. HAM and DOUGLAS showed how the apparatus could
be used for measurements on a substance less dense than water.

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[1] D. R. BRIGGS, *Ind. Eng. Chem.* (*Anal. Ed.*), 1940, 12, 703.
[2] A. J. HAM and W. HODGSON, *Trans. Faraday Soc.*, 1942, 38, 216, 407. F.
FAIRBROTHER and H. MASTIN, *J. Chem. Soc.*, 1924, 2319.

The second technique involves the use of single capillaries the dimensions of which can be measured directly. The method requires great care since the effects are smaller than those obtained with a plug. It is also limited to substances which can be made in the form of capillary tubes. RUTGERS and DE SMET[1] used this method to measure the electro-osmosis of salt solutions in glass capillaries. Three capillaries are mounted on a rotating cylindrical reservoir so that measurements can be made in triplicate. One of these capillaries and its mount are shown in Fig. 121. It is cleaned by filling and flushing out repeatedly with

(a)   (b)
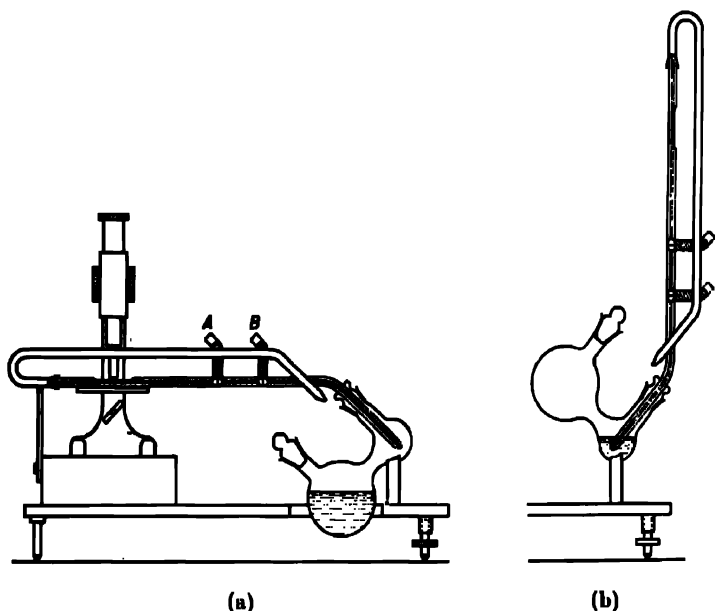
Fig. 121 Electro-osmosis cell[1]

solution in the vertical position. The measurements are carried out in the horizontal position by applying about 600 v. across the electrodes (A.B) and observing the movement of the meniscus in the microscope. The solution is kept under nitrogen and the conductance is checked before and after the experiment to ensure that it has undergone no change.

[1] A. J. RUTGERS and M. DE SMET, *Trans. Faraday Soc.*, 1945, 41, 758, 761.

(c) *Streaming potentials*

The apparatus required for measurement of streaming potentials is similar to that used for electro-osmosis. MARTIN and GORTNER[1] clamped the diaphragm under investigation (C) between perforated gold electrodes (E_1, E_2) (see Fig. 122). Excess pressure was applied by means of purified air and the potential measured using a qua-
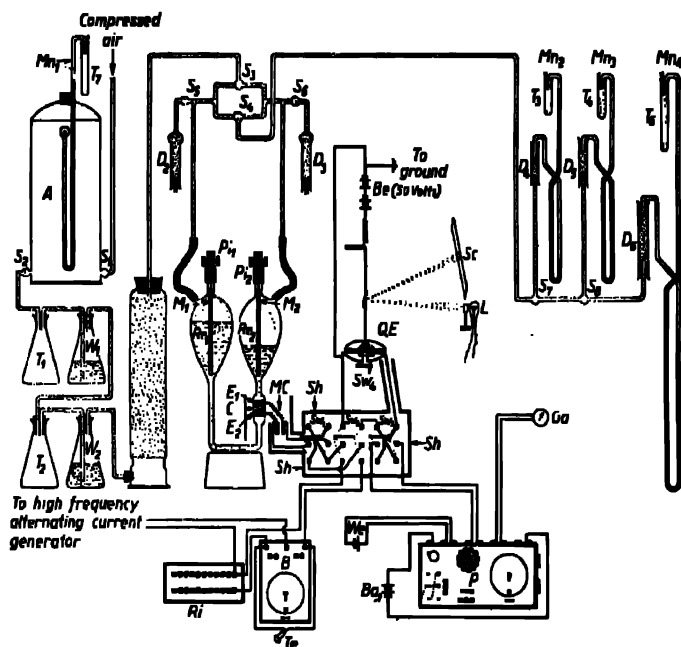
Fig. 122. Streaming potential cell. Reproduced from *J. Phys. Chem.*, 1930, 34, 1513

drant electrometer (QE) in conjunction with a potentiometer (P) (see also LAUFFER and GORTNER[2] for improved type of cell).

JONES and WOOD[3] have used single silica capillaries for the measurement of streaming potentials with very dilute aqueous solutions of electrolytes. By using a similar apparatus made entirely of vitreous silica, WOOD[4] was able to measure streaming potentials using very pure water. The usual reversible electrodes

[1] W. M. MARTIN and R. A. GORTNER, *J. Phys. Chem.*, 1930, 34, 1509.

[2] M. A. LAUFFER and R. A. GORTNER, *ibid.*, 1938, 42, 641.

[3] G. JONES and L. A. WOOD, *J. Chem. Phys.*, 1945, 13, 106.

[4] L. A. WOOD, *J. Am. Chem. Soc.*, 1946, 68, 437.
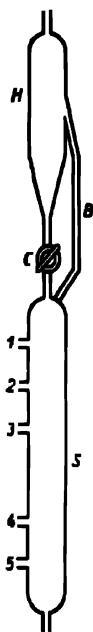
Fig. 123.
Sedi-
mentation
potential
cell [*]

could not be used owing to contamination of the water with ions, but no polarisation was observed at the smooth platinum electrodes used. This was probably due to the very low conductance which permitted only minute currents to flow.

(d) *Sedimentation potentials*

Sedimentation potentials may be studied by observing the potentials between electrodes placed at different heights in a column of fluid in which particles are falling. Early measurements appear unsatisfactory but recent measurements of Quist and Washburn[1] are less so.

These authors used a glass cell (Fig. 123) consisting of two vertical cylindrical compartments joined by a tap. The upper (H) held the powder which flowed through the tap (C) into the lower (S) which was provided with a series of non-polarisable electrodes (Ag | AgCl) spaced down the tube. (1, 2, 3, 4, 5).

9. Irreversible Electrode Phenomena (XI - 2)

Much of the work on irreversible electrode phenomena leads to results of obscure significance owing to an inadequate conception of the experimental requirements. This subject will be described with principal reference to hydrogen overpotential, since it is in this section of the subject that the technique has become most highly developed.

(i) *The Cell*

The essential requirements [2] of an electrolytic cell for the measurement of hydrogen overpotential are that it should, (I) maintain a hydrogen atmosphere against atmospheric oxygen, (II) maintain catholyte separate from the anolyte and from the

[*] Reproduced from *J. Am. Chem. Soc.*, 1940, **62**, 3169.

[1] J. D. Quist and E. R. Washburn, *J. Am. Chem. Soc.*, 1940, **62**, 3169.

[2] J. O'M. Bockris, *Chem. Rev.*, 1948, **43**, 526.

hydrogen electrode and (iii) be provided with a Luggin[1] capillary (preferably adjustable) connected with the reference electrode compartment. In solutions of specific conductivity about 0·01 mho. cm.$^{-1}$ the use of such a tip is essential at current densities above 10^{-4} amp.cm.$^{-1}$. (iv) Allow the introduction of a cathode in a state of high surface purity. The cell should also be arranged so that the current density is uniform over the whole electrode surface[2]. It has been shown[3] that the presence of tap grease has a marked effect on the overpotential at mercury electrodes. Modern cells are, therefore, designed to hold a vacuum without the use of greased joints by using carefully ground glass joints and taps which are sealed with the solvent which is used inside the cell (see Fig. 124).
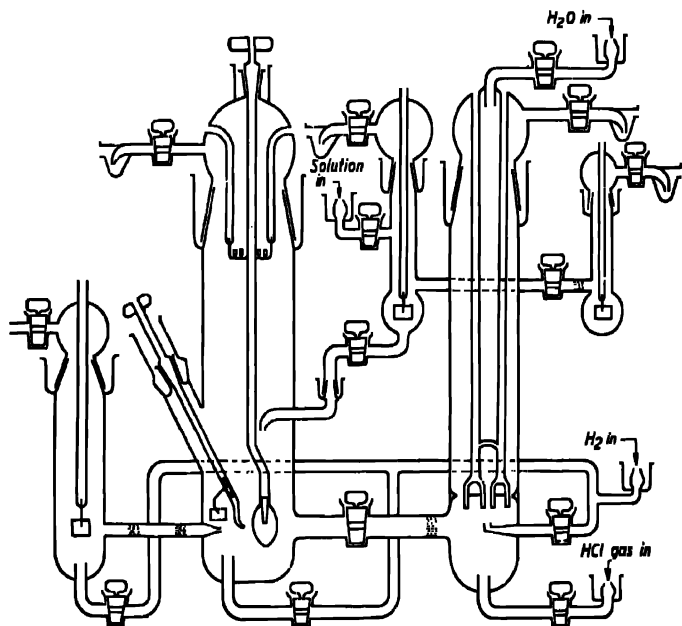
Fig. 124. Solid cathode overpotential cell.
Reproduced from *Chem. Rev.*, 1948, **43**, 528

[1] H. Luggin see F. Haber, *Z. physikal. Chem.*, 1900, **32**, 193.
[2] C. Goodeve, *Faraday Soc. Discussion*, 1947, **1**, 189.
[3] S. Levina and W. Sarinsky, *Acta Physicochim.*, U.S.S.R., 1937, **6**, 491.

(ii) *The Preparation of Solution*

The solution is prepared from reagents which are deoxygenated inside a closed apparatus connected to the cell. The most satisfactory electrolytes are those which can be produced in the gaseous state; for example, hydrochloric acid can be purified more readily than sulphuric acid. BOCKRIS and PARSONS [1] refluxed water under a reduced pressure of hydrogen for about 2 hours and then distilled it into the anode compartment of the cell until the specific conductance was about $8 - 5 . 10^{-7}$ mho cm.$^{-1}$. *Hydrogen chloride gas* was prepared by the action of pure sulphuric acid on potassium chloride which had been baked out in hydrogen at 550 °C. to remove traces of organic impurities. The gas was further purified by cooling to —80° in traps immersed in alcohol-solid carbon dioxide mixture, and passed into the water in the anode compartment of the cell, the concentration of the solution being measured conductometrically. However, even solutions prepared in this way have been found to contain traces of impurities which affect the electrode reaction. These impurities are best removed by a *"pre-electrolysis"* of the solution using an auxiliary cathode of the same material as the working cathode. In this way trace impurities are either reduced, deposited or adsorbed at the auxiliary cathode. A technique of this kind was first used empirically by LEWIS and JACKSON [2] followed by others, but only recently has a quantitative and theoretical study been made of this important method (BOCKRIS et al. [3]).

Electrolytic hydrogen was passed through the apparatus continuously (after initial evacuation to remove oxygen) during the preparation and the pre-electrolysis. The hydrogen was purified by passage through various absorbing agents, followed by a furnace at 400 °C. containing palladised asbestos to remove oxygen and then through a series of traps containing charcoal and glass wool at liquid air temperatures.

[1] J. O'M. BOCKRIS and R. PARSONS, *Trans. Faraday Soc.*, 1949, **45**, 916.

[2] G. N. LEWIS and R. F. JACKSON, *Z. physikal. Chem.*, 1906, **56**, 107. See also A. H. W. ATEN and M. ZIEREN, *Rec. Trav. Chim.*, 1929, **48**, 944; and Z. A. JOFA et al., *Acta Physicochim.*, *U.R.S.S.*, 1939, **10**, 817.

[3] A. M. AZZAM, J. O'M. BOCKRIS, B. E. CONWAY and H. ROSENBERG, *Trans. Faraday Soc.*, 1950, **46**, 918.

The preparation of alkaline solutions in a state of high purity is more difficult than that of acid solutions. KENYON used redistilled sodium, and LUKOVTSEV, LEVINA and FRUMKIN [1] used sodium amalgam. The latter method would appear to be suitable for work using mercury electrodes only. More recently POTTER [2] has obtained alkaline solution of suitable purity by repeated recrystallisation of the hydrated hydroxide, followed by prolonged electrolysis of the resulting solution. A general problem in work in alkaline solutions is connected with the possible deposition of the alkali metal onto the cathode.

(iii) *The Preparation of Electrodes*

Mercury cathodes may be obtained fairly readily in a high state of purity. BOCKRIS and PARSONS [1 p. 100] purified mercury by VON NARAY-SZÁBÓ's method [2 p. 100] and then distilled it twice in a HULETT still [3 p. 102]. Mercury electrodes also have the advantage that the cathode surface may be renewed a large number of times during the experiment, thus decreasing the danger of contamination with impurities deposited from the solution.

Solid cathodes are more difficult to prepare in a clean and reproducible state. Many types of preparation such as chemical attack, scraping, *etc.*, are unsatisfactory, since the electrode is exposed to the atmosphere before insertion in the solution, and during this time a grease or oxide film may be formed on the surface. A more *satisfactory method* is due to BOCKRIS and CON-WAY [3]. The wire cathode was maintained at a red heat for some time in a stream of pure hydrogen in a glass tube in which a thin bulb had been previously blown. During this process the electrode was sealed into the tube with about half the length of the wire projecting into the bulb. The tube was then sealed to a glass joint supported in the cathode compartment cap (Fig. 124) after which the cell is evacuated, filled with hydrogen, and the solution prepared as described above. The electrode is thus cooled in a hydrogen atmosphere and maintained therein during the preparation and pre-electrolysis of the solution, and, by breaking the bulb, it is brought into contact with the purified solution at

[1] H. F. KENYON, *Thesis*, Cambridge, 1936. P. LUKOVTSEV, S. LEVINA and A. N. FRUMKIN, *Acta Physicochim., U.S.S.R.*, 1939, 11, 1.

[2] E. C. POTTER, *Thesis*, London, 1950.

[3] J. O'M. BOCKRIS and B. E. CONWAY, *J. Sci. Instr.*, 1948, 19A, 28.

the appropriate moment. For clarity the cell illustrated has only one cathode, but the cells used in practice have several cathodes prepared in the above manner. The bulb surrounding each is broken in turn and after use the electrode can be raised above the level of the solution.

(iv) *The Method of Measurement*

A discussion of the direct and indirect methods of measurement of overpotential has been given above (p. 398). Since the indirect method is of particular use when a resistive film on the electrode surface is suspected [3 p. 402] and requires special apparatus, the latter will be described here.

Fig. 125a. Modern apparatus for indirect measurement of overpotential [1]

Circuit of Thyratron potentiometer
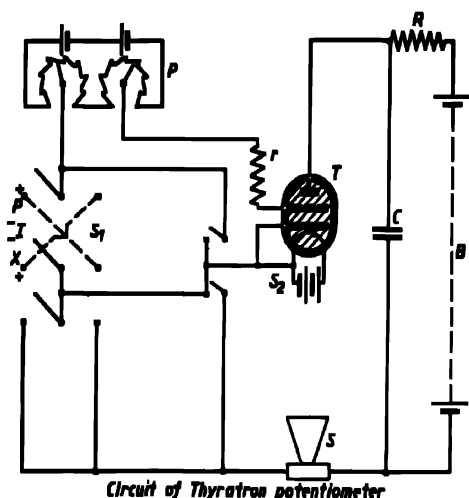
Fig. 125b. Modern apparatus for indirect measurement of overpotential [1]

The principle of the indirect method is to measure the potential while the current is switched off for a short time and extrapolate this measured potential difference back to the moment of interrupting the current. Early mechanical *commutators* were unsatisfactory for this purpose but an electronic device proposed by HICKLING[1] appears to be more accurate and can be used up to c.d.s. of about 1 amp.cm.$^{-2}$ in normal aqueous solutions.

The *interrupter circuit* is

[1] A. HICKLING, *Trans. Faraday Soc.*, 1937, **33**, 1540; 1940, **36**, 1226.

illustrated in Fig. 125a. The battery (B) charges up the condenser
(C) through the resistance (r), until the anode of the thyratron
becomes sufficiently positive to cause the thyratron to become
conducting, and the condenser discharges through the resistance
(R). A strongly negative potential is thus given to the grid circuit
of the valve (V), which then interrupts the polarising current to
the cell. When the condenser has discharged, the potential differ-
ence across the thyratron becomes small and it ceases to con-
duct. The negative potential on the grid of V decays through
R and the cycle repeats. Thus, the current passed through the
cell is interrupted, at intervals controlled by the resistance (r)
and the potentiometer (P), for a length of time controlled by
the resistance (R).

The lowest potential reached by the electrode during the
interruption is measured using a second thyratron circuit (Fig.
125b), in which the "flash over" of the thyratron is primarily
controlled by means of the grid circuit. With the switch (S_2)
closed the grid potential is adjusted using P until the thyratron
is just on the point of discharging, as indicated by the slow
succession of ticks from the loudspeaker (S). The e.m.f. from the
cell (X) and an ordinary potentiometer are introduced into
the grid circuit and the potentiometer is adjusted until the rate
of thyratron discharge is the same as before, (*i.e.* slow ticking
in the loudspeaker). Under these conditions the maximum value
of the sum of the unknown and potentiometer voltage is zero.
Thus, the reading on the potentiometer gives the minimum
value of the potential difference between the reversible electrode
and the working electrode in the cell. By adjusting the time
interval during which the current is interrupted, a series of po-
tentials at different times after switching off the current are
obtained, and are extrapolated to zero time to obtain the working
electrode potential. The times of decay used by HICKLING were
from 10^{-5} to $2 \cdot 10^{-4}$ sec.

This method has been criticised by FRUMKIN [1] on the grounds
that the decay of overpotential is too rapid to permit accurate
extrapolation, but the results obtained by this method are in

[1] A. N. FRUMKIN, *Acta Physicochim.*, *U.R.S.S.*, 1943, 18, 23.

fairly good agreement with those obtained using the direct method under similar experimental conditions on lead, copper and nickel electrodes [1] and a direct comparison of the direct and thyratron commutator methods, made by BOCKRIS and CONWAY [2], on iron electrodes in $N/10$ aqueous HCl shows good agreement up to 10^{-2} amp.cm.[2]

(v) *The Variation of Overpotential with Time*

A *discrepancy in experimental technique* which causes much of the wide variation in reported results is the *method of obtaining the overpotential-current density relation*. Fundamentally, this arises from differences of opinion as to the cause of the variations of overpotential with time which occur with some metals. Authors who consider this time variation to be an intrinsic phenomenon of overpotential prefer to record the stationary value reached by the overpotential after a prolonged polarisation; those who consider it to be connected with the presence of impurities carry out the measurements as rapidly as possible. At cathodes, such as mercury, where little or no variation occurs the disagreement disappears. For the remaining cathode materials the final decision has not yet been made. However, experimentally it is found [3] that *much, though not all, of the variation disappears when the careful preparation of solution described above is used.*

Some disagreement is also expressed about the necessity for keeping the test electrode cathodically polarised throughout the experiment. However, it appears probable that dissolution products accumulating near the surface of an unpolarised electrode will affect its behaviour on further polarisation.

(vi) *Rates of Discharge Reactions*

DOLIN and ERSHLER [1, p. 559] using an a.c. bridge method (*cf.* section 8) determined the equivalent circuit of the platinum electrode-solution interface. The simplest circuit which will fit the experi-

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[1] J. O'M. BOCKRIS, *Trans. Faraday Soc.*, 1947, **43**, 417. *Faraday Soc. Discussion*, 1947, **1**, 182.

[2] J. O'M. BOCKRIS and B. E. CONWAY, *J. Phys. Chem.*, 1949, **53**, 527.

[3] J. O'M. BOCKRIS and B. E. CONWAY, *Trans. Faraday Soc.*, 1949, **45**, 989.

mental results is that shown in Fig. 126, where $C_{d.l.}$ is the double layer capacity. By comparing the equations for the electrical circuit with rate equations for processes occurring at the electrode, these authors have shown that the resistance (R) is inversely proportional to *the rate of the neutralisation process*, which may thus be separated from the overall reaction.

A similar type of measurement has been made by RANDLES [1] of the *rate of discharge of metal ions on their dilute amalgams*. This author used an oscillographic method in which the potential difference across the cell and the phase angle were compared with the corresponding quantities across a standard resistance and capacity in parallel, by observing the LISSAJOUS figures formed when these potential differences were applied to the X and Y plates of the oscillograph (*cf.* p. 535).

Fig. 126.
Equivalent circuit

HEYROVSKÝ [2] also studied *slow deposition reactions* by observing the wave form across a polarographic cell polarised with square waves. Small kinks in the potential-time curves are observed when the ions are deposited or the metal ionizes. If the deposition and ionisation occur at the same potential the reaction may be considered to be reversible; if not it is irreversible. Unlike the above methods this has not so far led to quantitative results.

10. High Temperature Methods [3]

Electrical conductance and transport measurements form a particularly fertile method of approach to the problem of the state of molten substances, *e.g. silicates*. Measurements of the temperature coefficient and magnitude of conductivity, the nature of the current voltage relations, applicability of FARADAY laws, *etc.*, provide information on the degree of ionic conduction, the relative contributions of cationic and anionic processes to con-

[1] J. E. B. RANDLES, *Faraday Soc. Discussion*, 1947, 1, 11.

[2] J. HEYROVSKY, *ibid.*, 212.

[3] J. A. KITCHENER and J. O'M. BOCKRIS, *Faraday Soc. Discussion*, 1948, 4, 91.

duction, and the nature of the entities present in the melt [1].

Experimentally it is important that the *furnace* used should provide a uniform temperature zone round the cell, a controlla-
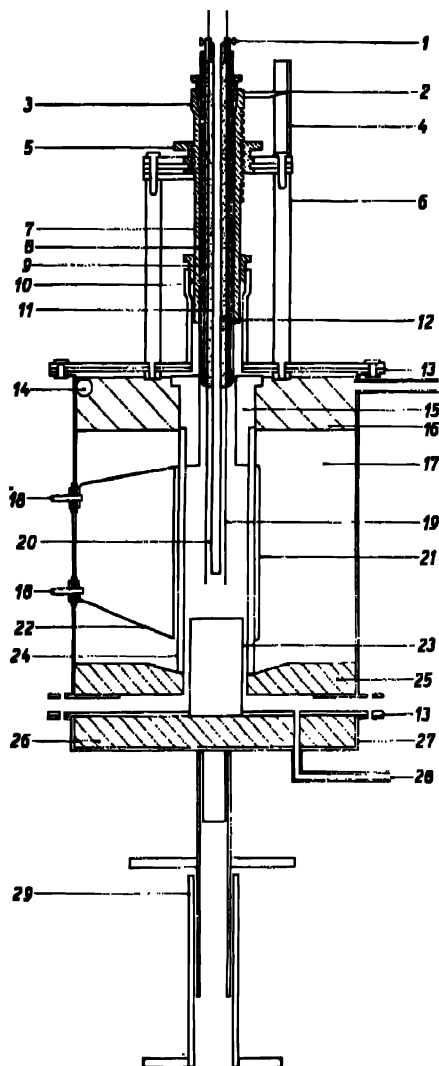
Diagram of Construction of Tube-type Molybdenum Furnace

1. Electrode clamp.
2. Pointer.
3. Gas-tight gland, asbestos packed.
4. Centimetre scale.
5. Gear for raising and lowering electrodes.
6. Support for lifting gear.
7. Brass tube.
8. 2" alumina tube.
9. 0·2 cm. molybdenum electrodes.
10. Gas-tight gland asbestos packed.
11. ½" alumina tube.
12. Alumina cement.
13. Uralite sheet.
14. Hydrogen inlet tube.
15. Alumina cement plug.
16. HT₁ brick.
17. Calcined alumina powder.
18. Terminals.
19. Molybdenum electrodes.
20. Sighting tube (molybdenum).
21. Winding (details not shown).
22. Tails of winding.
23. Alumina cement pedestral.
24. 4" alumina tube.
25. Firecrete cement base to furnace.
26. Firecrete cement.
27. Removable bottom of furnace.
28. Hydrogen outlet.
29. Gear for raising and lowering furnace bottom.

Fig. 127. Molybdenum resistance furnace.

Reproduced from *Faraday Soc. Discussion*, 1948, **4**, 95

[1] H. BLOOM and E. HEYMANN, *Proc. Roy. Soc.*, A, 1947, **188**, 392.   J. O'M. BOCKRIS, J. A. KITCHENER, S. IGNATOWICZ and J. W. TOMLINSON, *Faraday Soc. Discussion*, 1948, **4**, 265.   J. O'M BOCKRIS and J. W. TOMLINSON, *Research*, 1949, **2**, 362.

ble temperature and atmosphere. Of the two types of furnaces fulfilling these requirements, the *high frequency induction type* leads to less trouble with refractories than the *resistance type* since the crucible and/or contents only are heated. However, electrical measurements cannot so easily be made while the h.f. current is flowing and, if it is switched off, cooling is very rapid. Thus, the resistance type appears to be preferable for investigations of conductance. The resistance windings used are: nichrome (up to 1150 °C.) platinum (up to 1500°), molybdenum and tungsten (up to 2000° and 2500° respectively); the last two require a reducing atmosphere. Correspondingly the refractories used are: glass (up to 750°); quartz (up to 1200°); mullite, $2Al_2O_3 . 2SiO_2$ (up to 1700° in oxidising or 1600° in reducing atmospheres); alumina (up to 1900°); zircon (up to 2000° in oxidising or 1850° in a reducing atmosphere) and carbon (up to 2700°, or 3000 °C. for brief periods). *The measurement of temperature* is made with thermocouples, principally platinum, platinum-rhodium, which extend the range to 1400 - 1600 °C. At higher temperatures it is necessary to use optical pyrometers. A *typical resistance* furnace [1,p.603] for use in measurement of conductance up to 1800 °C. is shown in Fig. 127. The tube is of alumina, wound with molybdenum tape kept in a reducing atmosphere, usually forming gas (hydrogen-nitrogen mixtures). An adjustable assembly (5) permits the electrodes (19) to be lowered into the molybdenum crucible, it also supports a cylindrical sheath of molybdenum having a flat end (20). This is placed a few millimetres above the melt and the pyrometer is sighted on to the bottom, which has a temperature within two or three degrees of the melt. In this way the radiating surface approximates closely to a true black body and interference from the fumes from the melt is eliminated, thus making possible measurements of temperature accurate to $\pm 5°$ at 1800 °C.

At *lower temperatures* the more usual type of *glass or quartz cell* may be used (BLOOM and HEYMANN [1,p.604]) but above 1000 °C. *a platinum or molybdenum crucible* * contains the melt and acts

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* Molybdenum can be easily welded in a reducing atmosphere to form apparatus of various shapes [1].

[1] J. W. TOMLINSON and J. O'M. BOCKRIS, *Brit. Iron & Steel Research Ass.*, 1951, No. 38.

as one electrode, the other being a central wire. A WHEATSTONE bridge with a WAGNER earth (see section 6) is used, and a very pure sine wave is essential. At 1800 °C. the accuracy obtainable is only ± 5 - 10% because of the very high conductance, difficulty of temperature control, *etc. Polarisation* at such high temperatures is less than in aqueous solution and can be detected by examining the effect of changes in frequency and electrode area.

In *electrolysis measurements* the cell is generally of the U or H-tube type; if it cannot be made of glass or quartz, glass taps are attached to refractory vessels with PbO-glycerin cement. *Platinum or carbon anodes* are generally used. The products of electrolysis tend to dissolve back into the melt and away from the electrode, sometimes causing depolarisation [1]. Concentration changes near the electrode, thus tend to be eliminated by diffusion. Measurements are therefore often carried out only slightly above the melting point so that rapid solidification will preserve the concentration changes.

P. DROSSBACH, *Electrochemie geschmolzener Salze*, Berlin, 1938.

TABLES OF CERTAIN PHYSICO-CHEMICAL QUANTITIES *

The tables in the following chapter have been divided into four principal sets:

1. Universal physical constants and ratios.

2. Data concerning physical properties of chemical materials, e.g., refractivity, dipole moment.

8. Functions concerned in the physical chemistry of electrolytes, e.g., conductance, activity coefficients.

4. Data concerned with electrode processes, e.g., standard and redox electrode potentials and data on overpotential.

Where a full table of certain data has already appeared in previous chapters appropriate cross references have been given. In the tables an attempt has been made to specify the accuracy of the data. In some cases, however, this has been impossible owing to a lack of information in the original literature.

* By B. E. Conway, Ph. D. Imperial College of Science, London.

Note: The numbering of tables in this chapter is not continuous with that in the previous chapters of the book. The tables are numbered appropriately to the section of this chapter in which they appear.

1. Universal Constants and Ratios

TABLE I, 1
PRINCIPAL CONSTANTS AND RATIOS

Acceleration due to the earth's gravitational field	g_0 (Standard)	$= 980 \cdot 605$ cm.sec.$^{-1}$.
	g_{45}	$= 980 \cdot 616$ cm.sec.$^{-1}$ *.
Standard atmospheric pressure (the standard atmosphere)	A_0	$= (1 \cdot 013246 \pm 0 \cdot 000004) . 10^6$ dyne cm.$^{-2}$at.$^{-1}$
	A_{45}	$= (1 \cdot 013195 \pm 0 \cdot 000004) . 10^6$ dyne cm.$^{-2}$at.$^{-1}$
1 litre $= 1000$ ml.		$= 1000 \cdot 078 \pm 0 \cdot 002$ cc.
Volume of ideal gas (0 °C., A_0)		$= (22 \cdot 4146 \pm 0 \cdot 0006) . 10^3$ cm.^{3}mol^{-1}
		$= (22 \cdot 4140 \pm 0 \cdot 0006)$ litre.mol^{-1}
Volume of ideal gas (0 °C., A_{45})		$= (22 \cdot 4157 \pm 0 \cdot 0006) . 10^3$cm.^{3}mol^{-1}
		$= 22 \cdot 4151 \pm 0 \cdot 0006$ litre.mol^{-1}
Ice point		$= 273 \cdot 16 \pm 0 \cdot 01$ °K.
Normal calorie		$=$ Heat required to raise the temperature of 1 g. water from 14·5 to 15·5 °C.
Joule equivalent		$= 4 \cdot 1855 \pm 0 \cdot 0004$ abs.joule.cal.$^{-1}$
		$= 4.1847 \pm 0.0003$ int.joule.cal.$^{-1}$
Avogadro's Number, N_A		$= (6 \cdot 0228 \pm 0 \cdot 0011) . 10^{23}$ mol^{-1}
Specific gravity of mercury (0 °C., A_0) referred to air free water at its maximum density		$= 13 \cdot 59542 \pm 0 \cdot 00005.$
Density of mercury (0 °C., A_0)		$= 13 \cdot 59504 \pm 0 \cdot 00005$ g.cm.$^{-3}$
Planck's constant	h	$= (6 \cdot 624 \pm 0 \cdot 002) . 10^{-27}$ erg.sec.
Velocity of light in vacuum	c	$= (2 \cdot 99776 \pm 0 \cdot 00004) . 10^{10}$ cm. sec.$^{-1}$
The faraday	F	$= 96501 \pm 10$ int. coulomb/g.equiv.
(chemical scale) **		$\begin{cases} = 96487 \pm 10 \text{ abs. coulomb/g.equiv.} \\ = 9648 \cdot 7 \pm 1 \text{ e.m.u. coulomb/g.equiv.} \end{cases}$
	$F' = cF' = (2 \cdot 89247 \pm 0 \cdot 00030) . 10^{14}$ abs. e.s.u./g.equiv.	
F (physical scale) **		$= 96514 \pm 10$ abs.coul./g.equiv.
		$= 9651 \cdot 4 \pm 1$ abs.e.m.u./g.equiv.
		$= (2 \cdot 89326 \pm 0 \cdot 00030) . 10^{14}$ abs. e.s.u./g.equiv.
1 abs. electron volt $= 10^8 c_0 = 10^8 F/N_A = (1 \cdot 60203 \pm 0 \cdot 00034) . 10^{-12}$ erg.		
Energy in cal./mole for 1 e.v./molecule $= 23052 \pm 3$ cal.mol^{-1}		
Gas constant	R	$= (8 \cdot 31436 \pm 0 \cdot 00038) . 10^7$ erg.deg.$^{-1}$mol^{-1}
		$= 1 \cdot 98646 \pm 0 \cdot 00021$ cal.deg.$^{-1}$mol^{-1}
Boltzmann constant	$k = R/N_A = (1 \cdot 38047 \pm 0 \cdot 00026) . 10^{-16}$ ergs.deg.$^{-1}$.	

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* Suffices 0 and 45 refer to 0° and 45° of latitude respectively.

** In the "chemical scale" the equivalent weight is defined with reference to the normal isotopic mixture: $^{16}O + {}^{17}O + {}^{18}O = 16 \cdot 00000$, whilst on the physical scale it is defined with reference to the isotope $^{16}O = 16 \cdot 00000$.

TABLE I, 1 (*Continued*)

Electrochemical equivalents:

$$Ag = 1·11800 . 10^{-3} \text{ g./int.coulomb.}$$
$$= (1·11807 \pm 0·00012) . 10^{-3} \text{ g./abs.coulomb.}$$
$$I = (1·315026 \pm 0·000025) . 10^{-3} \text{ g./int.coulomb.}$$
$$= (1·31585 \pm 0·00014) . 10^{-3} \text{ g./abs.coulomb.}$$

International volt	= that potential difference which applied across a conductor of resistance one int.ohm causes a current of one int.ampère to flow.
International ohm	= Resistance opposed to a constant current by a column of mercury at 0 °C., 14·4521 g. in mass, of constant cross-sectional area and 100·300 cm. in length.
Coulomb (practical unit)	= Quantity of electricity transferred by a current of 1 ampère flowing for 1 second.
International ampère	= that uniform current which will deposit 0·00111800 g. Ag per second from a standard $AgNO_3$ solution.

For definitions of absolute electrostatic and electromagnetic units of charge etc., see Table I, 2.

International amp.	=	$0·99980 \pm 0·00002$ abs.amps.
,,	ohm	= $1·00048 \pm 0·00002$ abs.ohm.
,,	coulomb	= $0·99980 \pm 0·00002$ abs.coulomb.
,,	henry	= $1·00048 \pm 0·00002$ abs.henry.
,,	volt	= $1·00034 \pm 0·00003$ abs.volt.
,,	joule	= $1·00020 \pm 0·00004$ abs.joule.

Atomic wt. of electron $= F/e_0^{-}/m_e = (5·4862 \pm 0·0017) . 10^{-4}$ (physical scale),

or $(5·4847 \pm 0·0017) . 10^{-4}$ (chemical scale).

Mass of electron $m_e = e_0^{-}/e_0^{-}/m_e = (F/N_A)/e_0/m_e = (9·1066 \pm 0·0032) . 10^{-28}$ g.

Mass of H atom $= H/N_A = (1·67339 \pm 0·00031) . 10^{-24}$ g.

Mass of proton $= (1·67248 \pm 0·00031) . 10^{-24}$ g.

Ratio $\dfrac{\text{Mass H atom}}{\text{Mass electron}} = 1837·5 \pm 0·5.$

Ratio $\dfrac{\text{Mass proton}}{\text{Mass electron}} = 1836·5 \pm 0·5.$

Specific charge of proton $= e_0^{-}/\text{mass of proton} = 9578·7 \pm 1·0$ abs.e.m.u.g.$^{-1}$.

Electron charge $e_0^{-} = F/N_A = (1·60203 \pm 0·00034) . 10^{-20}$ abs.e.m.u.

$= (4·8025 \pm 0·0010) . 10^{-10}$ abs.e.s.u.

Specific electron charge $e_0^{-}/m_e = (1·7592 \pm 0·0005) . 10^{7}$ abs.e.m.u.g.$^{-1}$.

$= (5·2736 \pm 0·0015) . 10^{17}$ abs.e.s.u.g.$^{-1}$.

Ratio of e.s.u.: e.m.u. units of electrical charge =

c = velocity of light, (see above).

$h/e_0^{-} = (4·1340 \pm 0·0007) . 10^{-7}$ erg.sec.$^{-1}$e.m.u.$^{-1}$.

$= (1·3703 \pm 0·0002) . 10^{-17}$ erg.sec.e.s.u.$^{-1}$.

References:

R. T. BIRGE, *Rev. Mod. Phys.*, 1941, 13, 233.

See also:

U. STILLE, *Z. Physik*, 1943, 121, 24.

H. L. CURTIS, *J. Res. Nat. Bur. Stand.*, 1944, 33, 235.

TABLE

DIMENSIONS AND DEFINITIONS

Units are those proposed by the Report of the

A has the value 1 in e.s.u. or e.m.u. if ε and μ are

In e.s.u. $\varepsilon = 1$, $\mu = 1/c^2$.

ε and μ are connected by $\dfrac{1}{\mu\varepsilon} = c^2$ and $\varepsilon\mu = L^{-2}T^2$. m, L and T

Quantity	Symbol	Defining equation	Electrostatic unit	Electromagnetic unit
Charge	q	Force = $\dfrac{Aqq'}{\varepsilon r^2}$ $i = \dfrac{dq}{dT}$	Unit charge repels an equal charge 1 cm. away in vac. with force of 1 dyne.	Unit charge per sec. is delivered by unit current.
Current	i	$i = dq/dT$ $H = 2\pi a\,n\,i/r$ = magnetic field in coil of area a and radius r of n turns.	Unit current delivers unit charge/ sec.	Unit current flowing round 1 cm. arc of circle of radius 1 cm. produces unit magnetic field at centre.
Potential difference or e.m.f.	E or $\Delta\psi$	Energy = $E\,V$ Rate of working = $E\,i$	Unit e.m.f. confers on unit charge ability to perform 1 erg of work.	
Resistance	R	$E = i\,R$	Unit resistance allows unit e.m.f. to produce passage of unit current.	
Energy	w	w = force . distance	Unit energy is expended when 1 dyne acts through 1 cm.	
Power	Ψ	Power = dw/dT	Unit energy per sec.	
Capacity	C	Energy = $\dfrac{q^2}{2C}$	Conductor on which unit charge can be placed with expenditure of 1 erg of work.	

I, 2

OF ELECTRICAL UNITS

International Congress on Physics, London, 1934.

the dielectric constant and permeability of free space.

In e.m.u. $\varepsilon = 1/c^2$, $\mu = 1$.

are the standard notations for mass, length and time respectively.

Practical unit	Practical unit in		e.m.u. / e.s.u.	Dimensions of unit expressed in e.s.u.	Dimensions of unit expressed in e.m.u.
	e.s.u.	e.m.u.			
coulomb	$3 . 10^9$	10^{-1}	c	$\varepsilon^{1/2} m^{1/2} L^{1/2} T^{-1}$	$\mu^{-1/2} m^{1/2} L^{1/2}$
ampère	$3 . 10^9$	10^{-1}	c	$\varepsilon^{1/2} m^{1/2} L^{1/2} T^{-2}$	$\mu^{-1/2} m^{1/2} L^{1/2} T^{-1}$
volt	$^1/_3 . 10^{-2}$	10^8	$1/c$	$\varepsilon^{-1/2} m^{1/2} L^{1/2} T^{-1}$	$\mu^{1/2} m^{1/2} L^{1/2} T^{-2}$
ohm	$^1/_9 . 10^{-11}$	10^9	$1/c^2$	$\varepsilon^{-1} L^{-1} T$	$\mu L T^{-1}$
joule	10^7	10^7	1	$m L^2 T^{-2}$	$L^2 T^{-2}$
watt	10^7	10^{-9}	1	$m L^2 T^{-3}$	$\mu^{-1} L^{-1} T^3$
farad	$9 . 10^{11}$	10^{-9}	c^2	εL	

Quantity	Symbol	Defining equation	Electrostatic unit	Electromagnetic unit
Inductance	L	$E = L \, di/dT$		Conductor in which unit change of current/sec. produces unit e.m.f. has unit L.
Magnetic pole	m	Force $=$ $\dfrac{A}{\mu} \cdot \dfrac{mm'}{r^2}$		Unit pole repels equal pole 1 cm. away with force of 1 dyne.
Magnetic flux	Φ	$d\Phi/dT = -E$		Unit e.m.f. is induced in a circuit when Φ through it changes at the rate of 1 unit. (maxwell/sec.)
Magnetic induction or flux density	B	$\int B \, dS = \Phi$	Unit magnetic flux per cm.² (gauss)	
Magnetic field intensity	H	$\int H \, dl = 4\pi \, ani$ where l is the length of circuit carrying a current of i. Force on pole $m = mH$		Magnetomotive force round a circuit $=$ work done in taking unit pole round it $=$ line integral of magnetic field intensity $=$ force exerted on unit N pole; unit $= 1$ oersted.
Electric field intensity	F	$-F =$ differential of ψ with respect to distance	Space variation of potential or electric intensity $=$ force exerted on unit positive charge.	

(*Continued*)

Practical unit	Practical unit in		$\dfrac{\text{e.m.u.}}{\text{e.s.u.}}$	Dimensions of unit expressed in e.s.u.	Dimensions of unit expressed in e.m.u.
	e.s.u.	e.m.u.			
henry	$\frac{1}{9} \cdot 10^{-11}$	10^9	$1/c^2$	$\varepsilon^{-1}L^{-1}T^2$	μL
$4\pi \cdot 10^8$ maxwells $= 4\pi$ volt./sec.	$\frac{1}{3} \cdot 10^{-2}$	10^8	$1/c$	$\varepsilon^{-1/2}m^{1/2}L^{1/2}$	$\mu^{1/2}m^{1/2}L^{1/2}T^{-1}$
10^8 maxwells $= 1$ volt./sec.	$\frac{1}{3} \cdot 10^{-2}$	10^8	$1/c$	$\varepsilon^{-1/2}m^{1/2}L^{1/2}$	$\mu^{1/2}m^{1/2}L^{1/2}T^{-1}$
10^8 gauss $= 1$ volt sec./cm.²	$\frac{1}{3} \cdot 10^{-2}$	10^8	$1/c$	$\varepsilon^{-1/2}m^{1/2}L^{-1/2}$	$\mu^{1/2}m^{1/2}L^{-1/2}T^{-1}$
10^{-1} oersted	$3 \cdot 10^9$	10^{-1}	c	$\varepsilon^{1/2}m^{1/2}L^{1/2}T^{-2}$	$\mu^{-1/2}m^{1/2}L^{-1/2}T^{-1}$
volt/cm.	$\frac{1}{3} \cdot 10^{-2}$	10^8	$1/c$	$\varepsilon^{-1/2}m^{1/2}L^{-1/2}T^{-1}$	$\mu^{1/2}m^{1/2}L^{1/2}T^{-2}$

TABLE I, 8

CONVERSION FACTORS

ENERGY FACTORS

These are factors by which the given value must be multiplied to obtain that value in the sought units.

Given \ Sought	erg/ molecule	cm.$^{-1}$ $\left(\dfrac{1}{h.}\right)$/ molecule	e-volt/ molecule	cal./molecule
erg/molecule	1	$5 \cdot 048 \cdot 10^{15}$	$6 \cdot 252 \cdot 10^{11}$	$1 \cdot 441 \cdot 10^{16}$
cm.$^{-1}\left(\dfrac{1}{h.}\right)$/molecule	$1 \cdot 981 \cdot 10^{-16}$	1	$1 \cdot 239 \cdot 10^{-4}$	$2 \cdot 854$
e-volt/molecule	$1 \cdot 599 \cdot 10^{-12}$	$8 \cdot 074 \cdot 10^{3}$	1	$2 \cdot 304 \cdot 10^{4}$
cal./molecule	$6 \cdot 942 \cdot 10^{-27}$	$0 \cdot 3501$	$4 \cdot 340 \cdot 10^{-5}$	1

TABLE I, 8 (Continued)

PRESSURE FACTORS

(For method of use of these factors, see above)

Sought / Given	dyne/cm.²	g./cm.²	kg./m.²	mm. Hg	atmosphere	pound/in.²	pound/ft.²
dyne/cm.²	1	$1 \cdot 0198 \cdot 10^{-3}$	$1 \cdot 0198 \cdot 10^{-1}$	$7 \cdot 5010 \cdot 10^{-4}$	$9 \cdot 8697 \cdot 10^{-7}$	$1 \cdot 4504 \cdot 10^{-5}$	$2 \cdot 0887 \cdot 10^{-3}$
g./cm.²	980·6	1	10	$7 \cdot 3551 \cdot 10^{-1}$	$9 \cdot 6777 \cdot 10^{-4}$	$1 \cdot 4223 \cdot 10^{-2}$	2·0481
kg./m.²	98·06	10^{-1}	1	$7 \cdot 3551 \cdot 10^{-2}$	$9 \cdot 6777 \cdot 10^{-5}$	$1 \cdot 4223 \cdot 10^{-3}$	$2 \cdot 0481 \cdot 10^{-1}$
mm.Hg	1332	1·3595	13·595	1	$1 \cdot 3158 \cdot 10^{-3}$	$1 \cdot 9337 \cdot 10^{-2}$	2·7845
atmosphere	1,013,200	1033·8	10,333	760	1	14·696	2116·32
pound/in.²	68,944	70·308	703·12	51·715	$6 \cdot 8046 \cdot 10^{-2}$	1	144
pound/ft.²	478·78	$4 \cdot 883 \cdot 10^{-1}$	4·883	$3 \cdot 591 \cdot 10^{-1}$	$4 \cdot 7252 \cdot 10^{-4}$	$6 \cdot 945 \cdot 10^{-3}$	1

For accuracy of data see values quoted in Table I, 1.

Electrical Units: For conversion factors for electrical units see Table I, 2.

2. Data on Physical

TABLE

PHYSICAL CONSTANTS OF

Compound	Cryoscopic const. for 1 g.mol. in 1000 g. solvent	Ebullioscopic const. for 1 g.mol. in 1000 g. solvent	Viscosity in c.g.s. unit	Sp. conductance in mho.cm.$^{-1}$	Dielectric constant (static)
n-Pentane			0·002395 (20°)	$< 2 . 10^{-19}$ [47]	1·845 (20°) [32]
n-Hexane		2·83 [122]	0·00337 (15°)		1·904 (15°) [11]
n-Heptane			0·00333 (40°)		1·973 (20°) [109]
n-Octane		4·02 [82]	0·00542 (20°)		1·962 (20°) [109]
Cyclohexane	20·2 [34]	2·75 [27]	0·01056 (15°)		2·012 (25°) [171]
Benzene	5·227 [85]	2·587 [27]	0·00096 (15°)	5·32 – 4·48 . 10^{-17} (18°) [13]	2·2925 (15°) [85]
Toluene		3·33 [27]	0·00023 (15°)	1·4 . 10^{-14} [30]	2·3661 (25°) [166]

Properties

II, 1
SOME ORGANIC COMPOUNDS

Dipole moment in Debyes	Specific heat	Refractive index	Boiling pt. °C.	Freezing pt. °C.	Density $\left(\varrho\,\frac{t_1}{t_2}\right)$ †
0 [81]	0·54 (10·8 °C.) [97]	1·35746 D 20° [52]	36·00 [178]	—129·68 [178]	0·62632 20° 4°vac. [178]
0 [16]	0·53546 (17·71°) [98]	1·37486 D 20° [154]	68·71 [178]	—95·89 [178]	0·69545 20° 4°vac. [178]
0 [117]	0·527 (21·04°) [119]	1·38764 D (20°) [52]	98·4 [178]	—90·62 [178]	0·68865 20° 4° [178]
0 [53]	0·526 (25·14°) [98]	1·39748 D (20°) [154]	125·667 [178]	—56·798 [178]	0·69855 25° 4° [178]
0 [118] [152]	0·4411 (19·3°) [99]	1·42023 D (20°) [77]	80·738 [178]	6·554 [178]	0·77389 25° 4° [178]
0 [80] [152]	0·41441 (21·80°) [154]	1·50110 D (20°) [140]	80·103 [178]	5·533 [178]	0·87368 25° 4° [178]
0·4 [151]	0·4050 (25°) [155]	1·40682 D (20°) [140]	110·623 [178]	—94·991 [178]	0·86231 25° 4° [178]

TABLE II, 1

Compound	Cryoscopic const. for 1 g. mol. in 1000 g. solvent	Ebullioscopic const. for 1 g. mol. in 1000 g. solvent	Viscosity in c.g.s. unit	Sp.conductance in mho.cm.$^{-1}$	Dielectric constant static
Methanol		0·84 (⁸⁸)	0·00544 (25°) (⁴¹)	3 . 10^{-7} (25°) (¹⁸⁷)	31·2 (20°) (¹⁷⁹)
Ethanol	c. 3 (¹⁸)	1·20 ± 0·021 (¹³⁰)	0·01200 (20°) (¹⁵)	1·35 . 10^{-9} (25°) (⁸⁸)	25·00 (20°) (¹⁷⁹)
n-Propanol		1·59 (⁹)	0·019666 (25°) (¹⁴⁵)	9·17 . 10^{-9} (18°) (⁸³)	22·2 (20°) (¹⁷⁹)
Iso-Propanol			0·02430 (20°) (⁴⁶)	0·51 . 10^{-6} (25°) (¹⁶⁰)	13·8 (18°) (¹¹⁴)
n-Butanol			0·03378 (15°) (¹⁴¹)	9·12 . 10^{-9} (25°) (⁸³)	17·7 (17.2°) (²³⁹)
Iso-Butanol		2·01 (⁹)	0·04703 (15°) (¹⁴¹)	0·8 . 10^{-7} (25°) (¹⁵³)	17·95 (25°) (⁹)
Ethylene glycol			0·1733 (25°) (⁵¹)	1·16 . 10^{-6} (25°) (⁹⁰)	41·2 (20°) (¹⁸²)
Glycerol	3·27 - 3·69 (¹⁹⁸)		10·69 (20°) (¹)	0·9 . 10^{-7} (25°) (⁸¹)	15·3 (21°) (¹⁹)

(*Continued*)

Dipole moment in Debyes	Specific heat	Refractive index	Boiling pt. °C.	Freezing pt. °C.	Density $(\varrho\,{}_{4}^{t})$†
1·664 (188)	0·5966 (19·85°) (88)	1·35057 D (15°) (75)	64·75 (148)	—97·68 (129)	0·78662 25° 4° (42)
1·696 (89)	0·588 (24·9°) (95)	1·3614 D (20°) (21)	78·33 (28)	—114·49 (134)	0·785063 20° 4° (146)
1·65 (188) (89)	0·531 (18°) (94)	1·38543 D (20°) (21)	97·18 ± 0·01 (28)	—126·10 (95)	0·80835 20° 4° (79)
1·69 ± 0·035 (81)	0·596 (20°) (89)	1·37538 D (25°) (145)	82·258 (23)	—89·5 (157)	0·7830 25° (85)
1·06 (188)	0·505 (20·9°) (95)	1·39711 C (20°) (189)	117·72 ± 0·01 (59)	—90·2 (128)	0·81837 15° 4° (138)
1·79 (81)	0·716 (21°) (78)	1·3989 D (25°) (141)	108·10 (141)	—108·0 (96)	0·80576 15° 4° (141)
2·28 (129)	0·575 (19·0·) (90)	1·4320 D (16°) (75)	197·2 (129)	—12·3 (118)	1·113068 20° 4° (111)
	0·5795 (26·8°) (49)	1·47289 D (20°) (118)	290·6 (9)	18·18 (49)	1·2613 20° 4° (17)

TABLE II, 1

Compound	Cryoscopic const. for 1 g.mol. in 1000 g. solvent	Ebullioscopic const. for in g.mol. in 1000 g. solvent	Viscosity in c.g.s. unit	Sp. conductance in mho.cm.$^{-1}$	Dielectric constant static
Diethyl ether	1·79 [13]	2·16 [9]	0·00247 (15°) [141]	$\leqslant 8·7 . 10^{-13}$ (25°) [104]	4·376 (20°) [109]
1 : 4 Dioxane	4·8±0·3 [37]	3·27 [37]	0·01255 (25°) [57]	$5 . 10^{-15}$ (25°) [7]	2·235 (20°) [147]
Acetone	2·40 [84]	1·725 [87]	0·003371 (15°) [141]	$5·5 . 10^{-8}$ (25°) [104]	21·45 (20°) [80]
Formic acid	2·77 [171]	2·4 [9]	0·016376 (24·00°) [122]	$6·2 . 10^{-5}$ (25°) [120]	57·0 (21°) [94]
Acetic acid	3·9 [59]	3·075 (v. dry) [11]	0·01232 (20°) [44]	$11·2 . 10^{-9}$ (25°) [104]	6·13 (20°) [130]
Acetic anhydride		3·53 [11]	0·0110 (18°) [42]	$0·48 . 10^{-8}$ (25°) [151]	20·7 (18·5°) [152]

(*Continued*)

Dipole moment in Debyes	Specific heat	Refractive index	Boiling pt. °C.	Freezing pt. °C.	Density $(\varrho\,{}^{t_1}_{t_2})$ †	
1·15 ([87])	0·551 (16·84°) ([132])	1·35555 *D* (15°) ([141])	34·60 ([141])	—116·3 ([136])	0·71925 ([141])	15° 4°
0·45 ([113])	0·415 (18°) ([113])	1·4202 *D* (25°) ([55])	101·50 ([87])	11·65 ([71])	1·02802 ([113])	25° 4°
2·74±0·02 ([169])	0·5176 (20°) ([165])	1·36157 *D* (15°) ([141])	56·11 ([39])	—94·82 ([134])	0·78985 ([141])	20° 4°vac.
1·19 ([168])	0·5134 (17·66°) ([113])	1·37348 He (15°) ([159])	100·8 ([159])	8·40 ([44])	1·22647 ([159])	15° 4°
1·04 ([30])	0·488 (19·5°) ([59])	1·3698 *D* (25°) ([72])	118·10 ([18])	16·63 ([117])	1·04922 ([159])	20° 4°
2·8 ([177])	0·432 (23·56°) ([14])	1·39229 He (15°) ([159])	140·0 ([159])	—73·1 ([159])	1·0810 ([159])	20° 4°

TABLE II, 1

Compound	Cryoscopic const. for 1 g.mol. in 1000 g. solvent	Ebullioscopic const. for in g.mol. in 1000 g. solvent	Viscosity in c.g.s. unit	Sp. conductance in mho.cm.$^{-1}$	Dielectric constant static
Methyl acetate		2·061 [121]	0·00382 (20·3°) [8]	$1·923 . 10^{-4}$ (17°) [4]	8·016 (19.5°) [74]
Ethyl acetate		2·83 [21]	0·00424 (25°) [46]	$< 1 . 10^{-9}$ (25°) [70]	6·11 (20°) [72]
Ethyl chloride		1·95 [5]	$93·7 . 10^{-5}$ (0°)	$< 3 . 10^{-9}$ (0°) [176]	0·29 (170°, vapour in contact with liquid) [40]
Chloroform	4·90 [5]	3·66 - 3·91 [19]	0·00506 (15°) [140]	$< 10^{-10}$ (25°) [155]	4·6417 ± 0·01 (25°) [54]
Carbon tetrachloride	29·8 [13]	4·88 [7]	0·00958 (19·91°) [90]	$4 . 10^{-18}$ (18°) [47]	2·219 ± 0·002 (25°) [54]
Trichlorethylene	—	4·43 [155]	0·005490 (25°) [55]	Immeasurably small [155]	3·42 (10°) [85]
Nitrobenzene	6·89 [113]	5·27 [12]	0·0182 (25°) [154]	$1·22 . 10^{-8}$ (23·6°) [154]	34·098 ± 0·007 (25°) [54]
Carbon disulphide		2·35 [5]	0·00367 (20°) [123]	$\leqslant 3·7 . 10^{-8}$ (25°) [104]	2·6318 (20°) [86]

(Continued)

Dipole moment in Debyes	Specific heat	Refractive index	Boiling pt. °C.	Freezing pt. °C.	Density $\left(\varrho\,^{t_1}_{t_2}\right)$ †	
1·74 (¹⁵⁹)	0·502 (18·42°) (¹⁵⁹)	D (20°) 1·36148 (⁹⁶)	57·323 (¹³⁴)	—98·05 (¹³⁴)	0·9273 (¹³⁴)	25° 4°
1·81 (⁹²)	0·459 (20·44°) (¹⁴⁹)	D (20°) 1·37243 (⁷¹)	77·112 (¹³⁹)	—83·60 (¹⁷⁵)	0·90053 (¹³⁵)	20° 4°
2·05 (⁴⁵)	0·3036 (—28·59°) (¹⁰⁵)	D (0°) 1·3790 (¹⁴⁸)	12·28 (¹⁴⁹)	—138·30 (¹²⁵)	0·91708 (¹⁰⁰)	6° 6°
1·18 (⁹²)	0·2251 (19·9°) (¹¹⁰)	D (15°) 1·44858 (¹⁴⁰)	61·27 (¹⁴⁰)	—63·49 (¹³⁸)	1·49845 (¹⁴⁰)	15° 4°
0 (¹¹⁵)	0·2022 (19·9°) (¹¹⁰)	D (20°) 1·41040 (⁵⁰)	76·75 (⁵⁰)	—22·06 (¹²⁸)	1·58471 (⁵⁰)	25° 4°
0·8 (¹¹⁸)	0·223 (20°) (⁵³)	D (17°) 1·479141 (¹⁰⁶)	80·95 (¹³⁵)	—80·4 (¹²⁵)	1·4649 (⁵³)	20° 4°
4·24 (¹⁷⁸)	0·3442 (30°) (¹⁵²)	D (20°) 1·55261 (¹⁹)	209·6 (¹⁴⁴)	5·77 ± 0·02 (⁸⁴)	1·1983 (¹⁴⁴)	25° 4°
0 (¹⁷⁰)	0·242 (20°) (⁹⁸)	D (15°) 1·63189 (¹⁴¹)	46·25 (¹⁴¹)	—111·53 (¹⁴²)	1·2632 (⁹²)	20° 4°

TABLE II, 1

	Cryoscopic constant	Ebullioscopic constant	Viscosity in c.g.s. unit	Sp.conductance in mho.cm.$^{-1}$	Dielectric constant
Accuracy of figures in the respective columns.	$\pm 0.2 - \pm 0.8$	$\pm 0.08 - \pm 0.10$	$\pm 1\%$	$\pm 1\%$ but see SCHROEDER[*]	± 0.01 except where otherwise stated

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[*] N.B. SCHROEDER and JAFFÉ (1, 2) have shown that conductances of ordinarily pure organic materials may considerably be reduced by pre-electrolysis.

   [1]) J. SCHROEDER, *Ann. Phys.*, 1909, **29**, 125.

   [2]) G. JAFFÉ, *ibid.*, 1909, **28**, 326.

[†] Density; $\varrho \frac{20^\circ}{4^\circ}$ *for example* = density at 20 °C. relative to H_2O at 4 °C., where $t_1 = 20°$, and $t_2 = 4$ °C.; "vac" indicates corrected for vacuum.

Refractive indices: letters D, C and He refer to the Na_D Na_C and He_γ lines lines respectively used for the measurements.

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(Continued)

Dipole moment in Debyes	Specific heat	Refractive index	Boiling pt. °C.	Freezing pt. °C.	Density $(\varrho\,{}^t_4)$ †
± 0·1 Debye	±0·002— ±0·0005 for 4 sig. fig.	± 0·00004	± 0·02 —0·04	± 0·02 — 0·04	± 0·0005 — 0·00005

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TABLE II, 2.

ENTROPIES S_0 OF IONS IN AQUEOUS SOLUTION AT 25 °C.

(in cal.degree^{-1}. mol^{-1}), with reference to $S_{0,\,H^{\cdot}} = 0$

H·	0·00		Se···	—48 †		Ir····	—106	
Li·	4·7 ± 1·0		Y···	—34 †		U····	—67·9 †	
Na·	14·0 ± 0·4		Ga···	—69 †		OH'	2·49 ± 0·06	
K·	24·2 ± 0·2		In···	—42 †		F'	2·3 ± 2	
Rb·	28·7 ± 0·7		Tl···	—85 †		Cl'	13·50	†
Ca·	31·8 ± 0·6		As···	—60 †		Br'	19·7	†
NH4·	26·6 ± 0·6 *		Sb···	—43 †		I'	25·3	†
Ag·	17·54 ± 0·15		V···	—95 †		IO3'	28·0 ± 1·0	
Ag(NH3)2·	57·8 ± 1·0		Cr···	—65 †		HS'	14·9 ± 1·0	
Tl·	30·5 ± 0·4		Mn···	—59 †		HSO3'	32·6 ± 1·5	
Hg2··	19·7 ± 3		Fe···	—61 ± 5		SO3''	3 ± 3	
Be··	—27	†	Rh···	—60 †		HSO4'	30·6 ± 2	
Mg··	31·6 ± 3		Si····	—177 †		SO4''	4·4 ± 0·5 *	
Ca··	—12·7 ± 0·6 *		Ti····	—109 †		NO3'	29·9 ± 1	
Sr··	—7·3 ± 1·5		Ge····	—157 †		H2PO4'	21·6 ± 0·3 *	
Ba··	2·3 ± 0·3		Zr····	—81 †		HPO4''	8·7 ± 1·0 *	
Cu··	—26·5 ± 1·0		Sn····	—95 †		PO4'''	—52 ± 2 *	
Zn··	—25·7 ± 1·0		Pb····	—84 †		H2AsO4'	28 ± 1·0 *	
Cd··	—16·4 ± 1·5		Th····	—65 †		HCO3'	22·2 ± 0·8	
Sn··	—4·9 ± 1·0		V····	—114 †		CO3''	—13·0 ± 1·0	
Pb··	3·9 ± 0·9		Nb····	—101 †		C2O4''	9·6 ± 1·0	
Fe··	—25·9 ± 1·0		Mo····	—103 †		CN'	25 ± 5	
Co··	—27	†	Te····	—79 †		MnO4'	46·7 ± 0·4	
Ni··	—31	†	Ru····	—108 †		CrO4''	10·6 ± 1·0	
Mn··	—19·1	†	W····	—103 †				
Al···	—76 ± 10		Os····	—104 †				

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[1] For conversion to absolute entropies a value of S_0 for H· given by R. PARSONS and J. O'M. BOCKRIS (*Trans. Faraday Soc.*, 1951), as —4·0 e.u. may be used.

[2] Entropies of rare earth metal ions are given by A. F. KAPUSTINSKY (*loc. cit.*).

TABLE II, 3

TOTAL (ELECTRONIC + ATOMIC) POLARISABILITIES (a_0) OF IONS AND MOLECULES

Ion or molecule		$a_0 \cdot 10^{24}$ cm.^{3}	Ion or molecule		$a_0 \cdot 10^{24}$ cm.^{3}
Li˙	Ref. 1	0·075 ±0·02	Ce˙˙˙˙	Ref. 5	1·20
Na˙	,, 1	0·21 ±0·02	F′	,, 1	0·99 ±0·02
K˙	,, 1	0·87 ±0·02	Cl′	,, 2	3·02 ±0·02
Rb˙	,, 1	1·81 ±0·02	Br′	,, 1	4·17 ±0·02
Cs˙	,, 1	2·79 ±0·02	I′	,, 1	6·28 ±0·02
Cu˙	,, 5	1·81	O″	,, 5	2·70
Ag˙	,, 5	1·85 ±0·02	S″	,, 5	5·90
Be˙˙	,, 5	0·035	Se″	,, 5	6·42
Mg˙˙	,, 1	012 ±0·02	Te″	,, 5	9·00
Ca˙˙	,, 5	0·531	He	,, 1	0·20
Sr˙˙	,, 1, 5	1·42 ±0·02	Ne	,, 1	0·392
Ba˙˙	,, 5	1·69	A	,, 1	1·63
Cu˙˙	,, 5	0·670	Kr	,, 1	2·46
Zn˙˙	,, 5	0·114	Xe	,, 1	4·00
Cd˙˙	,, 5	0·96	Na	,, 3	29·7
Hg˙˙	,, 5	1·99	Hg	,, 3	10·43
Pb˙˙	,, 5	4·34	H$_2$	,, 4	0·787 ±0·02
Al˙˙˙	,, 1	0·065 ±0·02	O$_2$	,, 3	1·36 ±0·01
Se˙˙˙	,, 5	0·382	N$_2$	,, 3	1·73 ±0·02
Y˙˙˙	,, 5	1·02	CO	,, 4	1·844 ±0·02
La˙˙˙	,, 5	1·58	H$_2$O	,, 3	1·444 ±0·02
C˙˙˙˙	,, 5	0·012	H$_2$S	,, 3	3·642 ±0·02
Si˙˙˙˙	,, 1	0·034 ±0·02	SO$_2$	,, 3	3·774 ±0·02
Ti˙˙˙˙	,, 5	0·272	N$_2$O	,, 3	2·921 ±0·02
Zr˙˙˙˙	,, 5	0·800	O$_3$	,, 3	2·845 ±0·02

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TABLE II, 4

MOLAR REFRACTION R OF SALTS IN AQUEOUS SOLUTION AT 25 °C. AT INFINITE
DILUTION FOR THE WAVE LENGTH 5875·62 Å. (Na$_{D_1}$).

	NaCl	KCl	NaBr	$^1/_2$SrCl$_2$	NH$_4$NO$_3$	$^1/_2$Na$_2$SO$_4$
R cm.^{3}	9·282	11·296	12·825	19·080	15·817	7·547

Accurate to ±0·005 cm.^{3}

Ref. 1.

GRAM IONIC REFRACTION FOR IONS IN AQUEOUS SOLUTION AT 25 °C. AT
INFINITE DILUTION FOR WAVE LENGTH 5875·02 Å.

Ion	R cm.^{3}	Reference	Ion	R cm.^{3}	Refere
Na·	0·200	1	Cl′	9·032	1
K·	2·264	1	Br′	12·625	1
$^1/_2$Sr··	0·958	1	$^1/_2$SO$_4$″	7·847	1
$^1/_2$Ba··	2·185	2	F′	2·60	2
$^1/_2$Ca··	0·355	2	OH′	5·10	2
$^1/_2$Mg··	0·90	2	I′	19·23	1
NH$_4$·	4·30	1	ClO$_4$′	13·240	1
$^1/_2$Zn··	0·30	1	H$_2$O	3·7156	1

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See also L. PAULING, *Proc. Roy. Soc.*, 1927, 114 A, 181.

TABLE II, 5

CRYSTAL IONIC RADII OF ELEMENTS

Element	radii in Å	Element	radii in Å
H′	2·08 (2·08)	Ge·····	0·53 (0·76)
He	(0·93)	As·····	0·47 (0·71)
Li·	0·60 (0·60)	Se······	0·42 (0·66)
Be··	0·31 (0·44)	Br·······	0·39 (0·62)
B···	0·20 (0·35)	Ge‴′	2·72 (3·71)
C····	0·15 (0·20)	As‴	2·22 (2·85)
N·····	0·11 (0·25)	Se″	1·98 (2·32)
O······	0·09 (0·22)	Br′	1·95 (1·95)
F·······	0·07 (0·19)	Kr	(1·69)
C‴′	2·00 (4·14)	Rb·	1·48 (1·48)
N‴	1·71 (2·47)	Sr··	1·13 (1·32)
O″	1·40 (1·76)	Y···	0·93 (1·20)
F′	1·36 (1·36)	Zr····	0·80 (1·09)
Ne	(1·12)	Nb·····	0·70 (1·00)
Na·	0·95 (0·95)	Mo······	0·62 (0·93)
Mg··	0·65 (0·82)	Ag·	1·26 (1·26)
Al···	0·50 (0·72)	Cd··	0·97 (1·14)
Si····	0·41 (0·65)	In···	0·81 (1·04)
P·····	0·34 (0·59)	Sn····	0·71 (0·96)
S······	0·29 (0·53)	Sb·····	0·62 (0·89)
Cl·······	0·26 (0·49)	Te······	0·56 (0·82)
Si‴′	2·71 (3·84)	I·······	0·50 (0·77)
P‴	2·12 (2·79)	Sn‴′	2·94 (3·70)
S″	1·84 (2·19)	Sb‴	2·45 (2·95)
Cl′	1·81 (1·81)	Te″	2·21 (2·50)
Ar	(1·54)	I′	2·16 (2·16)
K·	1·33 (1·33)	Xe	(1·90)
Ca··	0·99 (1·18)	Cs·	1·69 (1·69)
Sc···	0·81 (1·06)	Ba··	1·35 (1·58)
Ti····	0·68 (0·96)	La···	1·15 (1·39)
V·····	0·59 (0·88)	Ce····	1·01 (1·27)
Cr······	0·52 (0·81)	Au·	1·37 (1·37)
Mn·······	0·46 (0·75)	Hg··	1·10 (1·25)
Cu·	0·96 (0·96)	Tl···	0·95 (1·15)
Zn··	0·74 (0·88)	Pb····	0·84 (1·06)
Ga···	0·62 (0·81)	Bi·····	0·74 (0·98)

Univalent crystal radii of ions are given in brackets. Accurate to ±1%.

L. PAULING, *J. Am. Chem. Soc.*, 1027, 49, 771; *Idem, Nature of the Chemical Bond,* Ithaca, 1948.

TABLE II, 6

INTERATOMIC COVALANT BOND DISTANCES IN Å.

	H 0·80			
	B	C	N	O	F
Single-bond radius	0·88	0·77	0·70	0·66	0·64
Double-bond ,,	0·76	0·67	0·61	0·57	0·55
Triple-bond ,,	0·68	0·60	0·55	0·51	

	Si	P	S	Cl
Single-bond radius	1·17	1·10	1·04	0·99
Double-bond ,,	1·07	1·00	0·95	0·90
Triple-bond ,,	1·00	0·93	0·88	

	Ge	As	Se	Br
Single-bond radius	1·22	1·21	1·17	1·14
Double-bond ,,	1·12	1·11	1·08	1·05

	Sn	Sb	Te	I
Single-bond radius	1·40	1·41	1·37	1·33
Double-bond ,,	1·30	1·31	1·28	1·24

Bond	Substance	Method [1]	One-half of obs. distance	Assigned * radius
C–C	Diamond	X-ray *	0·771	0·77
F–F	F_2 (g)	E.D. [2]	0·73	0·64
Si–Si	Si (c)	X-ray	1·17	1·17
P–P	P_4 (g)	E.D. [3]	1·10	1·10
P–P	P (c) (black)	X-ray [4]	1·09	1·10
S–S	S_8 (c)	X-ray [5]	1·05	1·04
S–S	S_8 (g)	E.D. [6]	1·05	1·04
Cl–Cl	Cl_2 (g)	Sp. *	0·992	0·99
Ge–Ge	Ge (c)	X-ray	1·22	1·22
As–As	As_4 (g)	E.D. [7]	1·22	1·21
As–As	As (c)	X-ray	1·25	1·21
Se–Se	Se (c)	X-ray	1·16	1·17
Br–Br	Br_2 (g)	Sp.	1·140	1·14
Sn–Sn	Sn (c) (grey)	X-ray	1·40	1·40
Sb–Sb	Sb (c)	X-ray	1·43	1·41
Te–Te	Te (c)	X-ray	1·38	1·37
I–I	I_2 (g)	Sp.	1·33	1·33

c ≡ crystal;   g ≡ gas.   Accuracy: ±1 - 3%.

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* See discussion in PAULING, *Nature of the Chemical Bond*, Ithaca, 1948.

TABLE II, 6 (*Continued*)

References:

[1] "X-ray" signifies the X-ray study of crystals, E.D. the electron-diffraction study of gas molecules, and Sp. the spectroscopic study of gas molecules.

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TABLE II, 7

ELECTRON WORK FUNCTIONS OF METALS

Metal	Electron Work Function in e.volt	Metal	Electron Work Function in e.volt	Metal	Electron Work Function in e.volt
Li	1·40	Cu	4·46	Tc	4·70
Be	3·10	Zn	3·66	Ba	1·73
Na	1·60	Ga	3·80	Ta	3·96
Mg	3·58	Ge	4·50	W	4·38
Al	3·38	Se	4·42	Os	4·55
K	1·00	Zr	3·60	Ir	4·57
Ca	3·38	Mo	4·48	Pt	4·52
Ti	4·14	Ru	4·52	Au	4·46
V	4·44	Rh	4·52	Hg	4·50
Cr	4·38	Pd	4·49	Tl	3·84
Mn	4·14	Ag	4·44	Pb	3·94
Fe	4·40	Cd	4·00	Bi	4·17
Co	4·21	Sn	4·09	Th	3·46
Ni	4·32	Sb	4·14	U	4·32

Accuracy: ±0·08 e.volt.

From O. KLEIN and E. LANGE, *Z. Elektrochem.*, 1938, **44**, 558.

TABLE II, 8

SUCCESSIVE IONISATION POTENTIALS I OF THE ELEMENTS IN ELECTRON VOLTS

Metal	$I_{Me^{\cdot}}$	$I_{Me^{\cdot\cdot}}$	$I_{Me^{\cdot\cdot\cdot}}$	$I_{Me^{\cdot\cdot\cdot\cdot}}$
Be	9·28	27·4	—	—
Mg	7·61	22·6	—	—
Al	5·96	24·1	53·0	—
Ca	6·09	17·9	—	—
Cr	6·74	23·8	50·3	—
Mn	7·89	23·1	—	—
Fe	7·88	24·8	—	—
Ni	7·61	25·8	—	—
Zn	9·86	27·2	—	—
As	10·5	30·6	58·8	—
Se	9·70	—	—	—
Sr	5·67	16·7	—	—
Mo	7·06	—	—	—
Cd	8·96	25·8	—	—
Sn	7·08	21·8	52·8	92·8
Ba	5·19	15·1	—	—
W	8·1	—	—	—
Pt	8·9	—	—	—
Pb	7·88	22·4	—	98·2

Accuracy: ±0·03 e.volt.

O. KLEIN and E. LANGE, Z. *Elektrochem.*, 1938, **44**, 561.

TABLE II, 9

DIELECTRIC CONSTANT OF WATER. VARIATION WITH TEMPERATURE

t °C.	ε	t °C.	ε	t °C.	ε
0	88·00	25	78·54	55	68·32
5	86·04	30	76·75	60	66·74
10	84·11	35	75·00	70	63·68
15	82·22	40	73·28	80	60·76
18	81·10	45	71·59	90	57·98
20	80·36	50	69·94	100	55·33

Values for the dielectric constant are accurate to ±0·15.

J. WYMAN, *Phys. Rev.*, 1930, **35**, 623.

See also J. WYMAN and E. N. INGALLS, *J. Am. Chem. Soc.*, 1938, **60**, 1182.

TABLE II, 10

DIELECTRIC CONSTANTS OF IONIC CRYSTALS

Substance	ε Static dielectric constant	ε_0 High frequency dielectric constant	Substance	ε Static dielectric constant
LiF	9·27	1·92	PbO	26
LiCl	11·05	2·75	PbS	18
LiBr	12·1	3·16	PbSO$_4$	14
LiI	11·03	3·80	Pb(NO$_3$)$_2$	17
NaF	6·0	1·74	PbCO$_3$	24
NaCl	5·62	2·25	CuO	18
NaBr	5·99	2·62	FeO	14
NaI	6·60	2·91	TiO$_2$	114
KF	6·05	1·85	SnO$_2$	24
KCl	4·68	2·13	HgCl$_2$	14
KBr	4·78	2·33	PbMoO$_4$	24
KI	4·94	2·69	Pb$_5$Cl(PO$_4$)$_3$	47·5
RbF	5·91	1·93		
RbCl	5·0	2·19		
RbBr	5·6	2·33	PbO to Pb$_5$Cl(PO$_4$)$_3$:	
RbI	5·0	2·63		*Reference 2.*
AgCl	12·3	4·01		
AgBr	13·1	4·62		
MgO	9·8	2·95		
CaO	11·8	3·28		
SrO	13·3	3·31		
CsCl	7·20	2·60		
CsBr	6·51	2·78		
CsI	5·65	3·03		
NH$_4$Cl	6·96	2·62		
TlBr	29·8	5·41		
TlCl	31·9	5·10		
CuCl	10·0	3·57		
CuBr	8·0	4·08		
ZnS	8·3	5·07		
BeO	7·35	2·95		
CaF$_2$	8·03	1·99		
SrF$_2$	7·69	2·08		
BaF$_2$	7·33	2·09		

LiF to BaF$_2$: *Reference 1.*

[1] K. HOJENDAHL, *Kgl. Danske Vidensk. Selskab*, 1938, 16, 2.
[2] F. C. FRANK, *Trans. Faraday Soc.*, 1937, 33, 513.

TABLE II, 11

DENSITY (ρ_t) OF FUSED SALTS AT TEMPERATURE $t°$ C.

given by $\rho_t = a - b \cdot 10^{-4} \cdot (t - t_1)$ where t and t_1 are in °C.

Compound	a (g./cc.)	b (g./cc./°C.)	t_1 °C.
LiF	1·798	4·4	850
LiCl	1·501	4·3	800
NaF	1·942	5·6	1000
NaCl	1·505	6·0	850
NaI	2·698	10·6	700
NaBr	2·306	7·2	780
NaOH	1·771	4·9	350
KF	1·878	6·69	900
KCl	1·530	5·947	750
KBr	2·106	7·99	750
KI	2·431	10·22	700
KOH	1·717	4·4	400
RbF	2·873	9·7	825
RbCl	2·252	8·7	714
RbBr	2·688	11·0	700
RbI	2·798	11·1	700
CsF	3·611	12·3	700
CsCl	2·786	10·8	650
CsBr	3·125	13·4	650
CsI	3·175	12·2	640
CuCl	3·677	7·9	422
Hg_2Cl_2	5·90	4·0	525
$HgCl_2$	5·118	3·38	240
$BeCl_2$	1·512	11·0	416
$MgCl_2$	1·086	2·9	712
$KCl . MgCl_2$	1·711	7·8	570
$CaCl_2$	2·03	4	850
$SrCl_2$	2·69	4·5	900
$BaCl_2$	3·12	0	1000
$ZnCl_2$	2·532	5·8	318
$ZnBr_2$	3·405	9·1	500
$CdCl_2$	3·32	6·9	600
$AlCl_3$	1·33	25	190
AlI_3	2·78	—	382
$AlBr_3$	2·26	—	265
$AlCl_3 . NH_3$	1·504	3·3	125
Na_3AlF_6	2·04	8·0	1035

TABLE II, 11 (*Continued*)

Compound	a (g./cc.)	b (g./cc./°C.)	t_1 °C.
$ScCl_3$	1·07	—	940
YCl_3	2·52	5	700
$LaCl_3$	3·155	5	860
$GaCl_3$	2·063	20·5	78
$GaBr_3$	3·138	29·5	125
GaI_3	3·600	22·4	211
$InCl_3$	2·14	21	586
$InCl_2$	3·05	16	235
$InCl$	3·74	14	225
$TlCl$	5·628	18	430
$ThCl_4$	3·8	—	765
$SnCl_2$	3·394	12	245
$PbCl_2$	4·947	16·4	500
$PbBr_2$	5·305	14·5	600
$SbCl_3$	2·671	21·7	75
$BiCl_3$	3·860	23·2	250
Na_2MoO_4	2·795	6·20	700
Na_2WO_4	$3·675 - 9·275\,(t - 930) + 3·37 \cdot 10^{-7}\,(t - 930)^2$		

No statement of the accuracy of these data is given.

P. DROSSBACH, *Electrochemistry of Fused Salts*, Berlin, 1938.

TABLE II, 12

DENSITIES (ρ_t) OF MOLTEN SALT MIXTURES. VALUES OF THE CONSTANTS a AND b IN THE EQUATION $\rho_t = a - b(t - 600)$

PbCl₂–CdCl₂ ($\pm 0 \cdot 2\%$) *

mol % PbCl₂	100	79·4	67·2	41·8	20·1	0
a	4·802 (4·768 LFJ)	4·544	4·388	4·018	3·698	3·366 (3·320 LFJ)
$b . 10^3$	1·50 (1·44 LFJ)	1·43	1·39	1·18	1·02	0·84 (0·69 LFJ)
Range in °C.	518 - 710	545 - 680	480 - 680	515 - 700	540 - 680	582 - 725

CdCl₂–CdBr₂ ($\pm 0 \cdot 1\%$)

mol % CdCl₂	100	70·8	54·4	34·7	0
a	3·366	3·598	3·709	3·832	4·040
$b . 10^3$	0·84	0·90	0·91	0·93	1·08
Range in °C.	582 - 725	580 - 680	590 - 710	606 - 705	580 - 720

CdCl₂–NaCl ($\pm 0 \cdot 2\%$)

mol % CdCl₂	100	77·8	64·8	55·5	44·8	34·8	0
a	3·366	3·108	2·919	2·768	2·574	2·398	(1·675)
$b . 10^3$	0·84	0·95	1·04	0·92	0·86	0·88	(0·68 J)
Range in °C.	582 - 725	560 - 700	540 - 680	570 - 680	500 - 690	580 - 690	Above 800

TABLE II, 12 (*Continued*)

PbCl₂–KCl (±0·6%)

mol % PbCl₂	100	82·1	68·8	47·4	0
a	4·802	4·288	8·745	8·282	(1·628 J)
$b \cdot 10^3$	1·50	1·42	1·28	1·18	(0·60 J)
Range in °C.	516 - 700	565 - 700	580 - 680	480 - 680	Above 750

PbCl₂–PbBr₂ (±0·15%)

mol % PbCl₂	100	80·8	49·7	15·4	0
a	4·802	4·928	5·095	5·264	5·848 (5·805 LFJ)
$b \cdot 10^3$	1·50	1·52	1·55	1·71	1·65 (1·45 LFJ)
Range in °C.	516 - 570	492 - 620	405 - 640	410 - 600	505 - 600

PbCl₂–AgCl (±0·10%)

mol % PbCl₂	100	80·6	70·9	61·1	58·4	42·6	20·8	0
a	4·802	4·790	4·782	4·778	4·775	4·764	4·789	4·698 (4·715 LH)
$b \cdot 10^3$	1·50	1·45	1·42	1·34	1·28	1·26	1·08	0·94 (0·92 LH)
Range in °C.	516 - 710	520 - 700	470 - 680	445 - 670	444 - 680	380 - 700	478 - 660	480 - 680

AgCl–AgBr (±0·15%)

mol % AgCl	100	77·8	59·7	34·2	0
a	4·698	4·875	5·006	5·190	5·402 (5·405 LH)
b . 10³	0·94	1·08	1·12	1·07	1·04 (1·08 LH)
Range in °C.	480 - 680	440 - 580	420 - 590	420 - 580	440 - 600

AgCl–KCl (±0·3%)

mol. % AgCl	100	80·6	68·0	47·8	0
a	4·698	3·898	3·425	2·758	(1·628 J)
b . 10³	0·94	0·05	0·96	0·88	(0·60 J)
Range in °C.	480 - 680	483 - 670	383 - 640	500 - 743	Above 750

AgBr–KBr (±0·25%)

mol % AgBr	100	79·2	60·1	39·5	0
a	5·400 (5·405 LH)	4·484	3·758	3·098	(2·226 J)
b . 10³	1·05 (1·08 LH)	1·12	1·08	0·98	(0·80 J)
Range in °C.	440 - 600	380 - 600	380 - 600	503 - 700	Above 750

TABLE II, 12 (Continued)

CdCl₂–KCl (±0·2%)

mol % $CdCl_2$	100	88·1	59·2	40·0	24·8	0
a	3·866	3·049	2·608	2·299	2·003	(1·628 J)
$b \cdot 10^3$	0·84	0·96	0·95	0·82	0·72	(0·60 J)
Range in °C.	582 - 725	584 - 700	464 - 680	460 - 680	604 - 750	Above 750

$PbCl_2$–$BaCl_2$

mol % $PbCl_2$	100	86·2	80·3	69·4	0
a	4·802	4·620	4·540	4·394	(3·850 AG)
$b \cdot 10^3$	1·50	1·85	1·86	1·27	(0·52 AG)
Range in °C.	516 - 710	565 - 700	575 - 690	660 - 710	Above 1000

$CdCl_2$–$BaCl_2$

mol % $CdCl_2$	100	82·9	54·0	45·8	0
a	3·866	3·488	3·480	3·493	(3·860 AG)
$b \cdot 10^3$	0·84	0·98	0·88	0·96	(0·52 AG)
Range in °C.	582 - 725	597 - 700	580 - 700	600 - 690	Above 1000

From N. K. BEARDMAN, F. H. DORMAN and E. HEYMANN, *J. Phys. and Colloid Chem.*, 1949, 53, 875.

Values in brackets by other authors

LFJ ≡ R. LORENZ, H. FREI and A. JABS, *Z. physik. Chem.*, 1907, 61, 468.
J ≡ F. M. JAEGER, *Z. anorg. Chem.*, 1917, 101, 175.
LH ≡ R. LORENZ and A. HOCHBERG, *ibid.*, 1916, 94, 305.
AG ≡ K. ARNDT and A. GESSLER, *Z. Elektrochem.*, 1908, 14, 665.

a is in the units g./cc. and b in g./cc./°C.

* Values in there brackets are accuracies of constants a and b.

TABLE II, 18

MOLAR VOLUMES OF MOLTEN SALT MIXTURES

$CdCl_2$–$CdBr_2$ (700 °C.) max. expt. error ±0·1%

| mol % $CdCl_2$ | 100 | 70·3 | 54·4 | 34·7 | 0 | | | |
| molar volume in cm.[3] | 55·88 | 59·79 | 61·88 | 64·52 | 69·28 | | | |

$PbCl_2$–$PbBr_2$ (600 °C.) max. expt. error ±0·15%

| mol % $PbCl_2$ | 100 | 80·3 | 49·7 | 15·4 | 0 | | | |
| molar volume in cm.[3] | 57·92 | 59·90 | 63·32 | 67·04 | 68·60 | | | |

$PbCl_2$–$AgCl$ (600 °C.) max. expt. error ±0·1%

| mol % $PbCl_2$ | 100 | 80·6 | 70·9 | 61·1 | 53·4 | 42·6 | 20·3 | 0 |
| molar volume in cm.[3] | 58·02 | 52·60 | 49·93 | 47·28 | 45·10 | 42·15 | 36·04 | 30·50 |

$AgCl$–$AgBr$ (600 °C.) max. expt. error ±0·15%

| mol % $AgCl$ | 100 | 77·3 | 59·7 | 34·2 | 0 | | | |
| molar volume in cm.[3] | 30·50 | 31·50 | 32·20 | 33·30 | 34·75 | | | |

$PbCl_2$–$CdCl_2$ (600 °C.) max. expt. error ±0·2%

| mol % $PbCl_2$ | 100 | 79·4 | 67·2 | 41·8 | 20·1 | 0 | | |
| molar volume in cm.[3] | 57·90 | 56·90 | 50·30 | 55·50 | 54·81 | 54·46 | | |

N. K. BOARDMAN, F. H. DORMAN and E. HEYMANN, *J. Phys. and Colloid Chem.*, 1949, **53**, 378.

TABLE II, 14

ELECTRICAL RESISTIVITIES (R_0) OF METALS AT $0\,°C.$ AND THEIR TEMPERATURE COEFFICIENTS α

$$\left[\alpha = \frac{1}{R_0} \cdot \frac{R_{100} - R_0}{100} ; \quad R_0 \text{ in ohm cm.}\ .\ 10^{-6} \right]$$

	R_0	α		R_0	α
Al	2·5	0·0043	Hg	94·07	— *
Sb	40	0·0050	Mo	5·7	0·0033
As	30	0·0039	Ni	6·7	0·0064
Ba	50 - 75	—	Nb	17	0·003
Be	12·2	—	Os	9·5	0·0042
Bi	115	0·0045	Pd	10·7	0·0037
Cd	7·7	0·0042	Pt	10·5	0·0030
Ca	~ 5	0·0088	K	6·7	0·0052 (0 °C.—m.p.)
C	~ 30	—	Re	21	0·0031
Ce	70	—	Rh	5	0·0046
Cs	19	0·0044	Rb	12·5	0·0052
Cr	14	—	Ru	14	—
Co	9·7	0·0033	Ag	1·6	0·0041
Cu	1·55	0·0043	Na	4·3	0·0055 (0 °C.—m.p.)
Ga	50	0·0040 (0 °C.—m.p.)	Sr	30	0·0038
Ge	~800	—	Ta	15	0·0031
Au	2·4	0·0034	Tl	17	0·0051
Hf	32	—	Th	18	—
In	8·3	0·0040	Sn	13	0·0045
Ir	5·3	0·0040	Ti	55	0·0054
Fe	10	0·0065	W	5·3	0·0048
La	55	—	U	~400	—
Pb	10	0·0042	V	~170	—
Li	8·5	0·0045	Zn	5·9	0·0041
Mg	4·4	0·0040	Zr	41	0·0044
Mn	~150	—			

* Temp. dependence is given by

$$R_t = 94·077 \cdot 10^{-6} [1 + 0·8862\ (t \cdot 10^{-3}) + 1·1057\ (t - 30) \cdot 10^{-6}],$$

where t is in °C.

Metals Reference Book, SMITHELLS, London, 1949.

3. Properties of Electrolytes and Electrolytic Solutions

TABLE III, 1

THE DEBYE-HÜCKEL EQUATION FOR AQUEOUS SOLUTIONS

Values of the constants in the equations

$$\log f_{\pm} = \frac{-A\sqrt{\Gamma_i}}{1 + B\sqrt{\Gamma_i}} \quad \text{and} \quad \log f_{\pm} = \frac{-A'\sqrt{c_i}}{1 + B'\sqrt{c_i}},$$

where the latter equation applies only for a *single* electrolyte, and the former equation is general for single or mixed electrolyte solutions of ionic concentration Γ_i or molarity c_i (where Γ is equal to $2I_{(m)}$, and $I_{(m)}$ is ionic strength).

$$\frac{B}{\ddot{a}} = \frac{\varkappa \cdot 10^{-1}}{\sqrt{\Gamma_i}} \quad \text{and} \quad \frac{B'}{\ddot{a}} = \frac{\varkappa \cdot 10^{-1}}{\sqrt{c_i}},$$

where $\ddot{a}$ is the mean distance of nearest approach of the ions measured in Å.

The valency factors w, w' and w'' are given by

$$w = \frac{1}{\nu} \sum_{1}^{\varrho} \ldots, \qquad w' = \frac{1}{\nu\sqrt{2}} \left\{ \sum_{1}^{\varrho} \nu_i z_i^2 \right\}^{1/2}, \qquad w'' = \left(\frac{1}{2} \bar{\Sigma}_1 \nu_i z_i^2 \right)^{1/2} = \frac{-}{-}$$

where ϱ is the number of types of ions derived from the electrolytic dissociation and ν is the number of ions resulting from this.

For binary electrolytes the factor w'' reduces to z ($= z_1 = z_2$)

T °C.	A	A'	B/$\ddot{a}$	B'/$\ddot{a}$
0	0·3446 w	0·4870 w'	0·2204	0·3244 w''
5	·3466	·4902	·2299	·3251
10	·3492	·4938	·2305	·3260
15	·3519	·4977	·2311	·3268
18	·3538	·5002	·2315	·3274
20	·3540	·5019	·2318	·3278
25	·3582	·5065	·2325	·3288
30	·3616	·5114	·2332	·3298
35	·3653	·5166	·2340	·3309
40	·3692	·5221	·2348	·3321
45	·3733	·5280	·2357	·3333
50	·3777	·5341	·2366	·3346
55	·3823	·5406	·2376	·3360
60	·3871	·5474	·2386	·3374
70	·3973	·5610	·2407	·3403
80	·4083	·5774	·2429	·3434
90	·4200	·5940	·2452	·3467
100	·4325	·6116	·2476	·3501

Errors in the limiting slopes A and A' do not exceed $\pm 0.1\%$. Errors in B and B' do not exceed $\pm 0.05\%$.

TABLE III, 1 (*Continued*)

EXTENDED TERMS OF THE DEBYE-HÜCKEL EQUATION

* The *extended terms* to be added to the first approximation equations for log $f_{\pm}$ on p. 645 are:

1. For symmetrical valence types:

$$\left(\frac{e_0^2 z^2}{\varepsilon k T a}\right)^2 [\tfrac{1}{4} X_3 x - 2 Y_3 x] + \left(\frac{e_0^2 z^3}{\varepsilon k T a}\right)^3 [\tfrac{1}{4} X_5 x - 4 Y_5 x] .$$

2. For unsymmetrical valence types:

$$- |z_1 z_2| \left\{ \frac{1}{(10^8 a)^2} (z_1 + z_2)^2 B_2 x - \frac{1}{(10^8 a)^3} (z_1^2 - |z_1 z_2| + z_2^2)(z_1 + z_2)^2 B_3^* x \right.$$
$$\left. - \frac{1}{(10^8 a)^2} (z_1^2 - |z_1 z_2| + z_2^2)^2 B_3 x \right\} .$$

Where,

$$B_2 x = \left(\frac{10^8 e_0^2}{\varepsilon k T}\right)^2 [\tfrac{1}{4} X_2 x - Y_2 x]$$

$$B_3^* x = \left(\frac{10^8 e_0^2}{\varepsilon k T}\right)^3 [\tfrac{1}{4} X_2' x - 2 Y_2']$$

and

$$B_3 x = \left(\frac{10^8 e_0^2}{\varepsilon k T}\right)^3 [\tfrac{1}{4} X_3 x - 2 Y_3 x] .$$

PARAMETERS INVOLVED IN THE EXTENDED TERMS* OF THE DEBYE-HÜCKEL THEORY

$x = \varkappa d$	$10^3 [\tfrac{1}{4} X_3 - 2 Y_3]$	$10^5 [\tfrac{1}{4} X_5 - 4 Y_5]$	$10^2 [\tfrac{1}{4} X_2 - Y_2]$	$10^3 [\tfrac{1}{4} X_2' - 2 Y_2']$
0·00	0·00000	0·00000	0·000000	0·000000
·005	—00092	—00107	—001482	·000009
·01	—00351	—00416	—004707	·000071
·02	—01239	—01487	—014784	·000423
·03	—02497	—02985	—027666	·001264
·04	—04014	—04725	—042363	·002693
0·05	—05711	—06564	—058209	·004750
·06	—07522	—08304	—074748	·007457
·07	—09403	—10138	—091660	·010809
·08	—11316	—11737	—108703	·014766
·09	—13231	—13153	—125699	·019291
0·10	—15130	—14363	—142514	·024335
·11	—16992	—15356	—15905	·02986
·12	—18802	—16126	—17522	·03580
·13	—20555	—16680	—19097	·04211
·14	—22240	—17028	—20626	·04874
0·15	—23853	—17166	—22105	·05563
·16	—25391	—17123	—23538	·06274
·17	—26851	—16910	—24908	·07002

* T. H. GRONWALL, V. K. LAMER and K. SANDVED, *Physik. Z.*, 1929, **29**, 358; V. K. LAMER, T. H. GRONWALL and L. J. GRIEFF, *J. Phys. Chem.*, 1931, **35**, 2245.

TABLE III, 1 (*Continued*)

$s = \kappa d$	$10^3 [\frac{1}{2}X_2 - 2Y_3]$	$10^5 [\frac{1}{2}X_5 - 4Y_3]$	$10^3 [\frac{1}{2}X_2 - Y_3]$	$10^3 [\frac{1}{2}X'_3 - ?$
·18	—28231	—16548	—26230	·07743
·19	—29530	—16087	—27497	·08493
0·20	—30750	—15409	—28710	·09248
·21	—31892	—14674	—29870	·10005
·22	—32953	—13847	—30977	·10761
·23	—33943	—12942	—32032	·11513
·24	—34859	—11973	—33036	·12258
0·25	—35708	—10953	—33991	·12994
·26	—36478	—09895	—34890	·13720
·27	—37187	—08804	—35755	·14433
·28	—37832	—07690	—36567	·15132
·29	—38416	—06577	—37335	·15816
0·30	—38942	—05453	—38060	·16482
·31	—39411	—04335	—38748	·17132
·32	—39827	—03222	—39386	·17762
·33	—40193	—02131	—39990	·18374
·34	—40510	—·01053	—40557	·18965
0·35	—40780	—00001	—41087	·19536
·36	—41007	+·01027	—41583	·20087
·37	—41193	+·02022	—42045	·20617
·38	—41339	+·02986	—42475	·21116
·39	—41448	+·03917	—42875	·21613
0·40	—41525	+·0481	—43244	·22080

TABLE III, 2

VALUES OF THE PARAMETER a IN THE DEBYE-HÜCKEL THEORY.

DISTANCES OF CLOSEST APPROACH IN NON-AQUEOUS SOLUTIONS

K = dissociation constant of the electrolyte in the solvent. Values of the distances of closest approach are calculated by the method of R. M. Fuoss and C. A. Kraus (*J. Am. Chem. Soc.*, 1933, **55**, 1019).

1. MeOH 25 °C.	From K	2. EtOH 25 °C.	From K
AgNO$_3$	2·36 Å.	KEtCO$_2$	2·47 Å.
Et$_4$NClO$_4$	2·66	Et$_4$NClO$_4$	2·57
Et$_4$NBr	4·86	Et$_4$N Picrate	3·65
KMeCO$_3$	4·98	KOEt	5·82
Et$_4$N Picrate	5·15	KI	5·87
KCl	7·54	LiI	10·08

A. G. Ogston, *Trans. Faraday Soc.*, 1936, **32**, 1679.

TABLE III, 3

VALUES OF THE PARAMETER a IN THE DEBYE-HÜCKEL THEORY.
DISTANCES OF CLOSEST APPROACH OF IONS IN AQUEOUS SOLUTIONS

Salt	Molality range fitted	a in Angstrom	Salt	Molality range fitted	a in Angstrom
HCl	0·01 - 1·0	4·47	MgCl₂	0·1 - 1·4	5·02
HBr	0·1 - 1·0	5·18	MgBr₂	0·1 - 1·0	5·46
HI	0·1 - 0·7	5·69	MgI₂	0·1 - 0·7	6·18
HClO₄	0·1 - 2·0	5·09	CaCl₂	0·01 - 1·4	4·73
LiCl	0·1 - 1·0	4·32	CaBr₂	0·1 - 1·0	5·02
LiBr	0·1 - 1·5	4·56	CaI₂	0·1 - 0·7	5·69
LiI	0·1 - 1·0	5·00	SrCl₂	0·1 - 1·8	4·61
LiClO₄	0·2 - 1·0	5·63	SrBr₂	0·01 - 1·4	4·89
NaCl	0·1 - 5·0	3·97	SrI₂	0·1 - 1·0	5·58
NaBr	0·1 - 4·0	4·24	BaCl₂	0·1 - 1·8	4·45
NaI	0·1 - 1·5	4·47	BaBr₂	0·1 - 1·5	4·68
NaClO₄	0·2 - 4·0	4·04	BaI₂	0·1 - 1·0	5·44
KCl	0·1 - 4·0	3·63	MnCl₂	0·1 - 1·4	4·74
KBr	0·1 - 4·0	3·85	FeCl₂	0·1 - 1·4	4·80
KI	0·1 - 4·0	4·16	CoCl₂	0·1 - 1·0	4·81
RbCl	0·1 - 1·5	3·49	NiCl₂	0·1 - 1·4	4·86
RbBr	0·1 - 1·5	3·48	Zn(ClO₄)₂	0·1 - 0·7	6·18
RbI	0·1 - 1·5	3·56			

From R. H. STOKES and R. A. ROBINSON, *J. Am. Chem. Soc.*, 1949, 70, 1870.
The data of J. H. JONES, *J. Phys. Chem.*, 1947, 51, 516, have been used for lithium
and sodium.

TABLE III, 4

MEAN ACTIVITY COEFFICIENTS $f_{\pm}$ OF ELECTROLYTES IN DILUTE AQUEOUS SOLUTION
(VALUES GIVEN AS $-\log_{10} f_{\pm}$)

Salt	Temp. °C.	Ref.	Molalities						
			0·0005	0·001	0·002	0·005	0·01	0·02	0·05
LiCl	Freezing	8	--	—	—	0·0343	0·0403	0·0005	0·0830
LiBr	point	8	—	—	—	0·0298	0·0400	0·0525	0·0720
LiNO₃	of the	1	—	—	—	0·0304	0·0412	0·0543	0·0760
LiClO₃	solution	4	—	—	—	0·0302	0·0406	0·0587	0·0745
LiClO₄	,,	4	—	—	—	0·0290	0·0386	0·0506	0·0602

TABLE III, 4 (*Continued*)

MEAN ACTIVITY COEFFICIENTS $f_\pm$ OF ELECTROLYTES IN DILUTE AQUEOUS SOLUTION
(VALUES GIVEN AS $-\log_{10} f_\pm$)

Salt	Temp. °C.	Ref.	Molalities						
			0·0005	0·001	0·002	0·005	0·01	0·02	0·05
LiOOC.H	Freezing	5	—	—	—	0·0311	0·0424	0·0573	0·0836
LiOOC.CH₃	point	5	—	—	—	0·0309	0·0421	0·0564	0·0799
	of the								
NaCl	solution	3	—	—	—	0·0306	0·0416	0·0557	0·0804
NaBr	,,	3	—	—	—	0·0282	0·0377	0·0503	0·0721
NaNO₃	,,	1	—	—	—	0·0311	0·0428	0·0584	0·0870
NaClO₃	,,	4	—	—	—	0·0310	0·0433	0·0588	0·0865
NaClO₄	,,	4	—	—	·-·	0·0321	0·0439	0·0588	0·0857
NaOOC.H	,,	5	—	—	—	0·0308	0·0416	0·0557	0·0794
NaOOC.CH₃	,,	5	—	—	·-·	0·0306	0·0412	0·0544	0·0754
KCl	,,	3	·-·	—	—	0·0317	0·0434	0·0587	0·0857
KBr	,,	3	—	—	—	0·0313	0·0428	0·0578	0·0839
KNO₃	,,	1	—	—	·-·	0·0329	0·0461	0·0645	0·1001
KClO₃	,,	4	—	—	—	0·0301	0·0418	0·0588	0·0918
KClO₄	,,	4	·-·	—	—	0·0347	0·0492	0·0697	—
KOOC.H	,,	5	—	·-·	—	0·0362	0·0406	0·0543	0·0774
KOOC.CH₃	,,	5	—	·-··	—	0·0306	0·0411	0·0544	0·0750
NH₄Cl	,,	2	·-·	—	—	0·0405	0·0555	0·0732	0·1025
NH₄Br	,,	2	·-·	—	—	0·0451	0·0605	0·0786	0·1082
NH₄I	,,	2	·-·	·-·	—	0·0375	0·0509	0·0074	0·0947
NH₄NO₃	,,	2	—	·-·	—	0·0401	0·0547	0·0736	0·1064
(NH₄)₂SO₄	,,	2	—	·-·	·-·	0·1308	0·1749	0·2204	0·3194

MEAN ACTIVITY COEFFICIENTS $f_\pm$ OF ELECTROLYTES IN DILUTE AQUEOUS SOLUTIONS

Salt	Temp. °C.	Ref.	0·0005	0·001	0·002	0·005	0·01	0·02	0·05
NaCl	25	6	—	—	—	0·0283	0·9032	0·8724	0·8215
LiOH	25	7	—	—	—	—	—	—	0·803
NaOH	25	8	·-·	—	—	—	—	·-·	0·818
KOH	25	9	—	—	—	·-·	—	·-··	0·824
CsOH	25	10	·-·	—	·-·	—	—	—	0·831
Na₂SO₄	0	11	—	—	—	—	0·719	—	0·537
H₂SO₄	0	12	0·908	0·873	0·825	0·734	0·649	0·554	0·420
H₂SO₄	25	12	0·885	0·830	0·757	0·639	0·544	0·453	0·340
SrCl₂	25	13	·-·	—	—	—	0·720	—	0·571
BaCl₂	25	13	—	—	—	—	0·723	—	0·554

TABLE III, 4 (*Continued*)

MEAN ACTIVITY COEFFICIENTS ($f_{\pm}$) OF ELECTROLYTES IN DILUTE AQUEOUS SOLUTIONS

Salt	Temp.° C.	Ref.	Molalities						
			0·0005	0·001	0·002	0·005	0·01	0·02	0·05
Ba(OH)$_2$	25	27	—	—	—	0·773	0·712	0·628	0·526
ZnCl$_2$	25	15	—	—	—	0·789	0·731	0·607	0·628
ZnBr$_2$	25	16	—	—	—	—	—	0·685	0·605
ZnI$_2$	25	17	—	—	0·851	0·799	0·746	0·690	0·621
ZnSO$_4$	25	22	0·780	0·700	0·608	0·477	0·387	0·298	0·202
CdCl$_2$	25	18	0·880	0·819	0·743	0·628	0·524	0·456	0·304
CdBr$_2$	25	19	0·855	0·787	0·699	0·570	0·468	0·370	0·259
CdI$_2$	25	20	—	—	—	0·490	0·370	0·281	0·167
CdSO$_4$	25	21	0·774	0·607	—	0·476	0·383	—	0·199
PbCl$_2$	25	14	0·902	0·850	0·803	0·704	0·612	0·497	—
AlCl$_3$	25	25/26	—	—	—	—	—	—	0·447
ScCl$_3$	25	25/26	—	—	—	—	—	—	0·447
LaCl$_3$	25	23	—	0·853	—	0·717	0·637	0·552	0·447
In$_2$(SO$_4$)$_3$	25	24	—	—	—	—	0·142	0·095	0·054
YCl$_3$	25	25/26	—	—	—	—	—	—	0·447
CeCl$_3$	25	25/26	—	—	—	—	—	—	0·447
PrCl$_3$	25	25/26	—	—	—	—	—	—	0·447
NdCl$_3$	25	25/26	—	—	—	—	—	—	0·447
SmCl$_3$	25	25/26	—	—	—	—	—	—	0·447
EuCl$_3$	25	25/26	—	—	—	—	—	—	0·447

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See also vol. I, Table 15, p. 161.

TABLES III, 5, 6 and 7
OSMOTIC AND ACTIVITY COEFFICIENTS OF ELECTROLYTES †

Osmotic and Activity Coefficients. The following tables * give practical osmotic and activity coefficients at 25°. Data have been included for one non-electrolyte, sucrose, [10], [11], [12] which should be useful as a reference solute for isopiestic measurements on other non-electrolytes, but data derived from isopiestic work on glycerol and urea [11] and an interesting series of measurements on 18 amino-acids [13] have been omitted. Some recent determinations on sodium and potassium acid sulphate [14] have also been omitted because, whilst the isopiestic data enable the vapour pressures to be calculated, the dissociation of the bisulphate ion makes f_v and $f_\pm$ values of little use. In addition, reference only is made to measurements [15] on a series of sodium salts of fatty acids up to the caprate.

The following notes will enable some estimate of the reliability of the data given in the tables to be made.

Some of the data depend on isopiestic measurements only and no confirmation is available from other techniques. This holds for the following salts: lithium iodide, perchlorate, nitrate, acetate and toluenesulphonate; sodium chlorate, perchlorate, bromate, nitrate, acetate, toluenesulphonate, thiocyanate and phosphate; potassium fluoride, chlorate, bromate, nitrate, acetate, toluenesulphonate, thiocyanate and phosphate; the five rubidium salts; caesium bromide, iodide, nitrate and acetate; silver nitrate; the three thallium salts, magnesium, manganese and nickel sulphate; all the trivalent metal salts (for lanthanum chloride independent isopiestic measurements are in good agreement); potassium ferrocyanide and ferricyanide; aluminium and chromium sulphate and thorium nitrate.

* For previous tabulations see refs. 5, 6 and 7.

† This compilation of values is taken from R. H. STOKES and R. A. ROBINSON, *Trans. Faraday Soc.*, 1949, **45**, 612.

TABLES III, 5, 6 en 7 (*Continued*)

With some it is possible to compare the osmotic and activity coefficients with those derived from freezing point measurements but there are seldom sufficient heat content data available to estimate the temperature correction exactly; nevertheless, it is found that the activity coefficients at $0.1m$ usually agree within 1% at the two temperatures; only in the case of lithium nitrate, potassium nitrate, potassium chlorate and sodium acetate do differences of up to 2% appear but the heat content data available are not sufficient to indicate if this difference is real or due to error in the activity coefficients at either temperature.

Hydrochloric Acid. The values of $f_\pm$ between 0.1 and $4m$ are taken from the very careful work of HARNED and EHLERS [16], interpolated at some concentrations by means of the DEBYE-HÜCKEL constants given by HARNED and EHLERS. Osmotic coefficients have been calculated by the method outlined by STOKES [9]. RANDALL and YOUNG [17] quote values of $f_\pm$ between 1.2 and $4m$ which are, on the average, 0.85% higher (*i.e.* a difference equivalent to 0.18 mv.). The data in the tables for concentrations above $4m$ are taken from the paper of RANDALL and YOUNG, some intermediate values being obtained by BESSELIAN interpolation. The values above $4m$ are supported by the data of ÅKERLÖF and TEARE [18] whose $f_\pm$ values exhibit an average deviation of 1% from those of RANDALL and YOUNG.

Hydrobromic Acid. The f_0 values are from HARNED, KESTON and DONELSON [19]; interpolation has been made at some concentrations by the use of their DEBYE-HÜCKEL constants and $f_\pm$ has been calculated by the procedure of STOKES [9].

Hydriodic Acid. The values depend on isopiestic data only [20].

Perchloric Acid. The isopiestic f_0 values agree within 1% with those derived from the direct vapour pressure measurements of PEARCE and NELSON [21]. Their $f_\pm$ values are, however, very different.

Nitric Acid. The $f_\pm$ values are those obtained from freezing point measurements by HARTMAN and ROSENFELD [42] with some interpolations added. The f_0 values are computed from these.

Lithium Hydroxide. $f_\pm$ values are from the e.m.f. measurements of HARNED and SWINDELLS [22] with interpolations at some concentrations.

Lithium Chloride and Bromide. The isopiestic data are confirmed up to $2m$ by the e.m.f. values of HARNED [23] which agree within 0.8% with the isopiestic values; above $2m$, however, there are considerable differences and, because the lithium amalgam electrode is known to be erratic, the isopiestic data are to be preferred.

Sodium Hydroxide. Up to $2m, f_\pm$ values interpolated from the e.m.f. measurements of HARNED [24] and of HARNED and HECKER [25] have been used; above $2m$ the isopiestic measurements of STOKES have been used [26]: it should be noted that the values of $f_\pm$ due to ÅKERLÖF and KEGELES [27] are considerably different (by about 3%).

Sodium Fluoride. Attention should be drawn to the e.m.f. measurements of IVETT and DE VRIES [28] which do not agree well with the $f_\pm$ values tabulated from isopiestic data.

Sodium Chloride. HARNED's [23] e.m.f. values of $f_\pm$ (extending up to $4m$) do not differ from those in the tables by more than 0.004 in $f_\pm$ at any concentration and

TABLES III, 5, 6 an 7 (*Continued*)

only differ on the average by 0·3%. Similar data by HARNED and NIMS [30] give an average difference of 0·5%, there being a difference of 0·009 in $f_\pm$ at 4m. The $f_\pm$ values of OLYNYK and GORDON [31] between 1·5 and 6m agree within 0·3% whilst f_0 values calculated from the direct vapour pressure measurements of NEGUS [31a] agree within 0·2% from 1 to 5m.

Sodium Bromide. The isopiestic data quoted in the tables agree within 0·2% with the e.m.f. data of HARNED and CRAWFORD [32] up to 2m; between 2·5 and 4m their data are higher by about 1·5%.

Sodium Iodide. The isopiestic data are in good agreement with the values quoted by HARNED [33], the average difference being 0·3% in $f_\pm$ up to 1m (the highest concentration at which e.m.f. measurements were made).

Potassium Hydroxide. Up to 4m values calculated from the e.m.f. measurements of HARNED and COOK [18] have been used and above 4m those of ÅKERLÖF and BENDER [34].

Potassium Chloride. The values quoted in the tables agree with those of HARNED [19] and of HARNED and COOK [35] with an average deviation of 0·4%. Moreover, the direct vapour pressure measurements of LOVELACE, FRAZER, and SEASE [35a] can be corrected from 20° to 25° to give values of f_0 which agree within 0·3%.

Potassium Bromide and Iodide. The values in the tables for the bromide, taken from isopiestic data, are within 0·3% of those given from e.m.f. data by HARNED [19]. Similarly, the data for the iodide agree within 0·3% up to 1m above which the e.m.f. values are 2% higher.

Caesium Hydroxide. The data quoted are derived from the e.m.f. measurements of HARNED and SCHUPP [36].

Caesium Chloride. The data in the tables, from isopiestic measurements, exhibit an average deviation of only 0·5% from the e.m.f. data of HARNED and SCHUPP.

Copper Sulphate. The e.m.f. data of NIELSEN and BROWN [37] are within 2% of the isopiestic $f_\pm$ values whilst the values of WETMORE and GORDON [38] are within 1·5%.

Zinc Sulphate. BRAY [39] has made measurements which yield activity coefficients which differ, on the average, by less than 2% from the isopiestic values quoted.

Cadmium Sulphate. The e.m.f. data of LAMER and PARKES [40] do not agree with the isopiestic values that have been used, there being differences of the order of 13%. Values at low molalities, enclosed in brackets, are subject to revision.

TABLE III, 5

OSMOTIC COEFFICIENTS AT 25 °C.

m	HCl	HBr	HI	HClO₄	HNO₃	LiOH	LiCl	LiBr	LiI	LiClO₄	LiNO₃
0·1	0·943	0·948	0·058	0·947	0·940	0·920	0·939	0·948	0·952	0·951	0·938
0·2	0·945	0·954	0·969	0·951	0·935	0·902	0·939	0·944	0·960	0·959	0·935
0·3	0·952	0·964	0·984	0·958	0·936	0·800	0·945	0·952	0·980	0·971	0·940
0·4	0·963	0·978	1·001	0·966	0·940	0·881	0·954	0·960	0·995	0·985	0·946
0·5	0·974	0·993	1·019	0·976	0·944	0·875	0·963	0·970	1·008	0·999	0·954
0·6	0·986	1·007	1·038	0·988	0·950	0·869	0·973	0·981	1·022	1·013	0·962
0·7	0·998	1·023	1·057	1·000	0·957	0·866	0·984	0·993	1·034	1·027	0·970
0·8	1·011	1·038	1·075	1·013	0·964	0·863	0·995	1·007	1·049	1·043	0·978
0·9	1·025	1·054	1·094	1·026	0·971	0·861	1·006	1·021	1·063	1·058	0·987
1·0	1·039	1·072	1·113	1·041	0·979	0·860	1·018	1·035	1·080	1·072	0·997
1·2	1·067	—	1·153	1·072	0·994	0·863	1·041	1·067	1·111	1·104	1·015
1·4	1·096	—	1·193	1·106	1·009	0·866	1·066	1·098	1·143	1·137	1·033
1·6	1·126	—	1·233	1·141	1·025	0·870	1·091	1·130	1·176	1·170	1·052
1·8	1·157	—	1·273	1·175	1·042	0·872	1·116	1·163	1·212	1·204	1·070
2·0	1·188	—	1·315	1·210	1·060	0·875	1·142	1·196	1·250	1·238	1·088
2·5	1·260	—	1·424	1·305	1·106	0·882	1·212	1·278	1·351	1·328	1·134
3·0	1·348	—	1·535	1·406	1·154	0·886	1·286	1·364	1·467	1·419	1·181
3·5	1·431	—	—	1·511	—	0·889	1·306	1·467	—	1·512	1·227
4·0	1·517	—	—	1·622	—	0·892	1·440	1·578	—	1·595	1·270
4·5	1·598	—	—	1·738	—	—	1·533	1·687	—	—	1·312
5·0	1·680	—	—	1·860	—	—	1·619	1·793	—	—	1·352
5·5	1·763	—	—	1·981	—	—	1·705	1·891	—	—	1·387
6·0	1·845	—	—	2·106	—	—	1·791	1·989	—	—	1·420
Ref.	16	10	20	41	42	22	10, 43	44, 45	10	46	47, 48

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TABLE III, 5 (Continued)

OSMOTIC COEFFICIENTS AT 25 °C.

m	$\overline{\text{LiAc}}$	$\overline{\text{LiTol}}$	NaOH	NaF	NaCl	NaBr	NaI	Na-ClO₃	Na-ClO₄	Na-BrO₃	Na-NO₃
0·1	0·935	0·928	0·925	0·924	0·932	0·934	0·938	0·927	0·930	0·918	0·921
0·2	0·928	0·917	0·925	0·908	0·925	0·928	0·936	0·913	0·920	0·896	0·902
0·3	0·929	0·912	0·929	0·898	0·922	0·928	0·939	0·904	0·915	0·883	0·890
0·4	0·931	0·908	0·933	0·891	0·920	0·929	0·945	0·897	0·912	0·873	0·881
0·5	0·935	0·906	0·937	0·886	0·921	0·933	0·952	0·892	0·910	0·865	0·873
0·6	0·940	0·906	0·941	0·882	0·923	0·937	0·959	0·888	0·909	0·857	0·867
0·7	0·945	0·905	0·945	0·879	0·926	0·942	0·967	0·885	0·910	0·851	0·862
0·8	0·951	0·905	0·949	0·876	0·929	0·947	0·975	0·883	0·911	0·845	0·858
0·9	0·956	0·905	0·953	0·874	0·932	0·953	0·983	0·882	0·912	0·839	0·854
1·0	0·962	0·905	0·958	0·872	0·936	0·958	0·991	0·880	0·913	0·833	0·851
1·2	0·975	0·904	0·969	—	0·943	0·969	1·007	0·878	0·916	0·824	0·845
1·4	0·988	0·902	0·980	—	0·951	0·983	1·025	0·876	0·920	0·815	0·839
1·6	1·001	0·899	0·991	—	0·962	0·997	1·043	0·874	0·925	0·808	0·835
1·8	1·014	0·894	1·002	—	0·972	1·012	1·061	0·875	0·930	0·804	0·830
2·0	1·027	0·893	1·015	—	0·983	1·028	1·079	0·876	0·934	0·800	0·826
2·5	1·061	0·899	1·054	—	1·013	1·067	1·129	0·879	0·947	0·792	0·817
3·0	1·093	0·912	1·094	—	1·045	1·107	1·188	0·881	0·960	—	0·810
3·5	1·123	0·930	1·139	—	1·080	1·150	1·243	0·886	0·975	—	0·804
4·0	1·153	0·951	1·195	—	1·116	1·199	—	—	0·991	—	0·797
4·5	—	0·972	1·255	—	1·153	—	—	—	1·008	—	0·792
5·0	—	—	1·314	—	1·192	—	—	—	1·025	—	0·788
5·5	—	—	1·374	—	1·231	—	—	—	1·042	—	0·787
6·0	—	—	1·434	—	1·271	—	—	—	1·060	—	0·788
Ref.	47	47	24, 25, 26, 27	29	2	44, 49	44	50	46	51	47

$\overline{\text{Ac}}$ = Acetate. $\overline{\text{Tol}}$ = Toluenesulphonate.

[1] G. N. LEWIS and M. RANDALL, Thermodynamics (McGraw-Hill Book Co. Inc., New York, 1923).

[6] E. A. GUGGENHEIM, Phil. Mag., 1935, 19, (7), 588; 1936, 22, (7), 322.

[7] H. S. HARNED and B. B. OWEN, Physical Chemistry of Electrolytic Solutions, Reinhold Publishing Corp., New York, 1943.

TABLE III, 5 *(Continued)*

OSMOTIC COEFFICIENTS AT 25 °C.

m	$\overline{\text{NaAc}}$	$\dfrac{\text{Na-}}{\text{Tol}}$	Na-CNS	NaH$_2$-PO$_4$	KOH	KF	KCl	KBr	KI	K-ClO$_3$	K-BrO$_3$	K-NO$_3$
0·1	0·940	0·924	0·937	0·911	0·944	0·930	0·927	0·928	0·932	0·918	0·910	0·906
0·2	0·939	0·907	0·934	0·884	0·936	0·919	0·913	0·916	0·922	0·887	0·881	0·873
0·8	0·945	0·897	0·935	0·864	0·938	0·915	0·906	0·910	0·918	0·867	0·858	0·851
0·4	0·951	0·887	0·938	0·847	0·944	0·914	0·902	0·906	0·917	0·849	0·837	0 833
0·5	0·959	0·880	0·943	0·832	0·953	0·915	0·899	0·904	0·917	0·832	0·816	0·817
0·6	0·907	0·874	0·948	0·819	0·962	0·916	0·898	0·904	0·918	0·816	—	0·802
0·7	0·977	0·867	0·953	0·808	0·972	0·910	0·897	0·904	0·910	0·802	—	0·790
0·8	0·980	0·861	0·958	0·798	0·983	0·923	0·897	0·905	0·922	—	—	0·778
0·9	0·994	0·855	0·963	0·789	0·993	0·926	0·897	0·906	0·924	—	—	0·767
1·0	1·002	0·849	0·969	0·780	1·003	0·931	0·897	0·907	0·926	—	—	0·756
1·2	1·018	0·837	0·979	0·765	1·026	0·941	0·899	0·910	0·931	—	—	0·736
1·4	1·038	0·824	0·990	0·751	1·051	0·951	0·901	0·914	0·937	—	—	0·718
1·6	1·057	0·811	1·002	0·739	1·076	0·962	0·904	0·917	0·943	—	—	0·700
1·8	1·074	0·799	1·014	0·729	1·100	0·973	0·908	0·922	0·950	—	—	0·684
2·0	1·092	0·787	1·025	0·721	1·125	0·984	0·912	0·927	0·957	—	—	0·669
2·5	1·137	0·763	1·055	0·705	1·183	1·014	0·924	0·941	0·974	—	—	0·631
3·0	1·181	0·748	1·086	0·696	1·248	1·048	0·937	0·955	0·990	—	—	0·602
3·5	1·223	0·738	1·118	0·691	1·317	1·084	0·950	0·969	1·006	—	—	0·577
4·0	—	0·733	1·150	0·691	1·387	1·124	0·965	0·984	1·021	—	—	—
4·5	—	—	—	0·694	1·459	—	0·980	1·000	1·032	—	—	—
5·0	—	—	—	0·699	1·524	—	—	1·015	—	—	—	—
5·5	—	—	—	0·706	1·594	—	—	—	—	—	—	—
6·0	—	—	—	0·718	1·661	—	—	—	—	—	—	—
Ref.	47	47	52	53	33, 34	29	2	44, 40	44, 54	51	55	47

$\overline{\text{Ac}}$ = Acetate.　$\overline{\text{Tol}}$ = Toluenesulphonate.

[8] M. RANDALL and A. M. WHITE, *J. Am. Chem. Soc.*, 1926, **48**, 2514.

[9] R. H. STOKES, *ibid.*, 1945, **67**, 1686.

[10] R. A. ROBINSON and P. A. SINCLAIR, *ibid.*, 1934, **56**, 1830.

[11] R. A. ROBINSON, P. K. SMITH and E. R. B. SMITH, *Trans. Faraday Soc.*, 1942, **38**, 63.

[12] G. SCATCHARD, W. J. HAMER and S. E. WOOD, *J. Am. Chem. Soc.*, 1938, **60**, 3061.

TABLE III, 5 *(Continued)*

OSMOTIC COEFFICIENTS AT 25 °C

m	$\overline{KAc}$	$\overline{KTol}$	K·CNS	KH₂-PO₄	RbCl	RbBr	RbI	Rb·NO₂	$\overline{RbAc}$	$\overline{CsOH}$	CsCl	CsBr
0·1	0·943	0·921	0·920	0·901	0·923	0·922	0·921	0·903	0·943	0·942	0·917	0·917
0·2	0·944	0·901	0·911	0·868	0·907	0·905	0·904	0·871	0·945	0·939	0·897	0·896
0·3	0·951	0·886	0·904	0·848	0·898	0·897	0·896	0·847	0·952	0·940	0·885	0·882
0·4	0·958	0·873	0·900	0·823	0·893	0·892	0·890	0·826	0·961	0·949	0·875	0·878
0·5	0·968	0·860	0·897	0·805	0·889	0·888	0·886	0·809	0·971	0·900	0·869	0·865
0·6	0·977	0·847	0·896	0·789	0·887	0·886	0·884	0·794	0·981	0·970	0·864	0·861
0·7	0·987	0·834	0·895	0·773	0·886	0·884	0·881	0·781	0·992	0·982	0·861	0·857
0·8	0·997	0·822	0·895	0·760	0·886	0·882	0·880	0·768	1·002	0·992	0·859	0·854
0·9	1·007	0·809	0·894	0·747	0·885	0·881	0·879	0·756	1·013	1·003	0·858	0·852
1·0	1·017	0·798	0·894	0·736	0·885	0·881	0·878	0·745	1·023	1·014	0·857	0·850
1·2	1·038	0·775	0·893	0·716	0·886	0·880	0·878	0·725	1·046	—	0·856	0·849
1·4	1·060	0·751	0·892	0·698	0·888	0·881	0·878	0·706	1·068	—	0·856	0·848
1·6	1·081	0·732	0·892	0·683	0·890	0·882	0·880	0·689	1·091	—	0·857	0·848
1·8	1·103	0·715	0·893	0·669	0·893	0·884	0·882	0·673	1·114	—	0·859	0·850
2·0	1·123	0·700	0·894	—	0·896	0·887	0·880	0·656	1·137	—	0·862	0·852
2·5	1·177	0·664	0·898	—	0·905	0·893	0·893	0·620	1·192	—	0·869	0·859
3·0	1·228	0·637	0·903	—	0·916	0·900	0·901	0·588	1·248	—	0·879	0·866
3·5	1·274	0·615	0·906	—	0·928	0·907	0·911	0·561	1·302	—	0·889	0·874
4·0	—	—	0·912	—	0·941	0·916	0·921	0·538	—	—	0·900	0·884
4·5	—	—	0·917	—	0·952	0·924	0·931	0·516	—	—	0·912	0·892
5·0	—	—	0·921	—	0·966	0·934	0·940	—	—	—	0·924	0·901
5·5	—	—	—	—	—	—	—	—	—	—	—	—
6·0	—	—	—	—	—	—	—	—	—	—	—	—
Ref.	47	47	52	53	10, 50	44, 56	44, 56	47, 56	47, 56	30	10, 86	44, 56

Ac = Acetate.   Tol = Toluenesulphonate.

[13] E. R. B. SMITH and P. K. SMITH, *J. Biol. Chem.*, 1937, 117, 209; 121, 607; 1940, 132, 47, 57.

[14] R. H. STOKES, *J. Am. Chem. Soc.*, 1948, 70, 874.

[15] P. K. SMITH and R. A. ROBINSON, *Trans. Faraday Soc.*, 1942, 38, 70.

[16] H. S. HARNED and R. W. EHLERS, *J. Am. Chem. Soc.*, 1933, 55, 2179.

[17] M. RANDALL and L. E. YOUNG, *ibid.*, 1928, 50, 989.

TABLE III, 5 (Continued)

OSMOTIC COEFFICIENTS AT 25 °C.

m	CaI	CaNO₃	C̄aAc	Ag-NO₃	Tl-ClO₄	Tl-NO₃	T̄lAc	CuSO₄	Mg-SO₄	ZnSO₄	CdSO₄
0·1	0·916	0·902	0·945	0·903	0·900	0·881	0·913	0·561	0·606	0·590	0·565
0·2	0·895	0·869	0·947	0·870	0·867	0·833	0·891	0·515	0·562	0·533	0·513
0·3	0·880	0·842	0·954	0·847	0·842	0·800	0·876	0·494	0·540	0·506	0·490
0·4	0·870	0·820	0·964	0·827	0·821	0·775	0·865	0·478	0·529	0·492	0·476
0·5	0·863	0·802	0·975	0·811	0·804	—	0·855	0·469	0·522	0·488	0·466
0·6	0·858	0·787	0·986	0·795	—	—	0·849	0·462	0·518	0·476	0·458
0·7	0·855	0·774	0·996	0·779	—	—	0·843	0·458	0·517	0·473	0·452
0·8	0·852	0·761	1·006	0·766	—	—	0·838	0·457	0·518	0·473	0·450
0·9	0·849	0·748	1·016	0·754	—	—	0·833	0·458	0·520	0·474	0·449
1·0	0·846	0·736	1·026	0·742	—	—	0·820	0·461	0·525	0·478	0·452
1·2	0·842	0·715	1·040	0·720	—	—	0·823	0·473	0·542	0·489	0·461
1·4	0·839	0·695	1·072	0·699	—	—	0·818	0·491	0·567	0·508	0·476
1·6	0·836	—	1·095	0·680	—	—	0·814	—	0·597	0·533	0·496
1·8	0·834	—	1·119	0·662	—	—	0·810	—	0·630	0·566	0·522
2·0	0·832	—	1·142	0·646	—	—	0·807	—	0·666	0·602	0·551
2·5	0·827	—	1·196	0·609	—	—	0·801	—	0·780	0·717	0·632
3·0	0·822	—	1·251	0·570	—	—	0·796	—	0·922	0·861	0·726
3·5	—	—	1·306	0·550	—	—	0·789	—	—	1·038	0·832
4·0	—	—	—	0·523	—	—	0·783	—	—	—	—
4·5	—	—	—	0·502	—	—	0·777	—	—	—	—
5·0	—	—	—	0·488	—	—	0·772	—	—	—	—
5·5	—	—	—	0·467	—	—	0·766	—	—	—	—
6·0	—	—	—	0·452	—	—	0·760	—	—	—	—
Ref.	44, 56	47, 56	47, 56	57	56	56	56	58	58	58	58

A̅c = Acetate.

[18] G. Åkerlöf and J. W. Teare, ibid., 1937, 59, 1855.
[19] H. S. Harned, A. S. Keston and J. G. Donelson, ibid., 1936, 58, 989.
[20] H. S. Harned and R. A. Robinson, Trans. Faraday Soc., 1941, 37, 302.
[21] J. N. Pearce and A. F. Nelson, J. Am. Chem. Soc., 1933, 55, 3075.
[22] H. S. Harned and F. E. Swindells, ibid., 1926, 48, 126.

TABLE III, 5 (*Continued*)

OSMOTIC COEFFICIENTS AT 25 °C.

m	Mn-SO$_4$	NiSO$_4$	AlCl$_3$	ScCl$_3$	CrCl$_3$	YCl$_3$	LaCl$_3$	CeCl$_3$	PrCl$_3$	NdCl$_3$	SmCl$_3$
0·1	0·587	0·581	0·819	0·797	0·811	0·789	0·788	0·782	0·784	0·783	0·789
0·2	0·538	0·533	0·841	0·827	0·833	0·810	0·800	0·805	0·801	0·801	0·809
0·3	0·516	0·508	0·889	0·868	0·875	0·847	0·833	0·835	0·830	0·832	0·841
0·4	0·501	0·488	0·947	0·917	0·926	0·892	0·871	0·872	0·866	0·871	0·879
0·5	0·490	0·475	1·008	0·969	0·983	0·939	0·912	0·914	0·905	0·913	0·921
0·6	0·481	0·465	1·074	1·027	1·045	0·989	0·955	0·955	0·945	0·954	0·964
0·7	0·475	0·458	1·145	1·090	1·111	1·042	0·998	1·007	0·996	1·006	1·019
0·8	0·472	0·456	1·220	1·156	1·181	1·100	1·052	1·057	1·046	1·056	1·074
0·9	0·472	0·456	1·299	1·222	1·250	1·161	1·102	1·107	1·100	1·110	1·128
1·0	0·475	0·459	1·382	1·291	1·310	1·223	1·154	1·158	1·154	1·165	1·186
1·2	0·485	0·472	1·500	1·430	1·443	1·354	1·266	1·264	1·271	1·283	1·302
1·4	0·504	0·492	1·749	1·572	—	1·491	1·384	1·387	1·388	1·404	1·427
1·6	0·527	0·517	1·951	1·718	—	1·631	1·502	1·504	1·507	1·527	1·554
1·8	0·556	0·551	2·175	1·869	—	1·780	1·623	1·638	1·631	1·656	1·686
2·0	0·588	0·589	—	—	—	1·940	1·748	1·777	1·759	1·789	1·824
2·5	0·677	0·708	—	—	—	—	—	—	—	—	—
3·0	0·782	—	—	—	—	—	—	—	—	—	—
3·5	0·909	—	—	—	—	—	—	—	—	—	—
4·0	1·048	—	—	—	—	—	—	—	—	—	—
Ref.	58	58	59	59	60	59	59, 61	59	59	59	62

[58] H. S. HARNED, *ibid.*, 1929, 51, 416.

[54] H. S. HARNED, *ibid.*, 1925, 47, 676.

[55] H. S. HARNED and J. C. HECKER, *ibid.*, 1933, 55, 4838.

[56] R. H. STOKES, *ibid.*, 1945, 67, 1689.

[57] G. ÅKERLÖF and G. KEGELES, *ibid.*, 1940, 62, 620.

TABLE III, 5 *(Continued)*

OSMOTIC COEFFICIENTS AT 25 °C.

m	EuCl$_3$	Cr(NO$_3$)$_3$	K$_3$Fe(CN)$_6$	K$_4$Fe(CN)$_6$	Al$_2$(SO$_4$)$_3$	Cr$_2$(SO$_4$)$_3$	Th(NO$_3$)$_4$
0·1	0·794	0·795	0·727	0·595	0·420	0·414	0·675
0·2	0·812	0·818	0·695	0·556	0·390	0·401	0·685
0·3	0·842	0·860	0·682	0·535	0·391	0·412	0·705
0·4	0·882	0·906	0·678	0·518	0·421	0·437	0·734
0·5	0·926	0·953	0·676	0·506	0·477	0·473	0·770
0·6	0·971	1·003	0·676	0·498	0·545	0·524	0·807
0·7	1·027	1·055	0·679	0·494	0·625	0·585	0·846
0·8	1·082	1·111	0·685	0·494	0·718	0·657	0·885
0·9	1·137	1·168	0·694	0·501	0·809	0·740	0·925
1·0	1·193	1·227	0·705	—	0·922	0·832	0·965
1·2	1·310	1·343	0·727	—	—	1·031	1·044
1·4	1·438	1·456	0·750	—	—	—	1·120
1·6	1·570	—	—	—	—	—	1·192
1·8	1·707	—	—	—	—	—	1·259
2·0	1·853	—	—	—	—	—	1·325
2·5	—	—	—	—	—	—	1·455
3·0	—	—	—	—	—	—	1·546
3·5	—	—	—	—	—	—	1·616
4·0	—	—	—	—	—	—	1·659
4·5	—	—	—	—	—	—	1·688
5·0	—	—	—	—	—	—	1·700
Ref.	62	60	63	56	56	60	63

[56] R. W. IVETT and T. DE VRIES, *ibid.*, 1941, **63**, 2821.

[59] R. A. ROBINSON, *ibid.*, 1941, **63**, 628.

[60] H. S. HARNED and N. F. NIMS, *ibid.*, 1932, **54**, 423; H. S. HARNED and M. A. COOK, *ibid.*, 1939, **61**, 495.

[61] F. OLYNYK and A. R. GORDON, *ibid.*, 1943, **65**, 224.

[61a] NEGUS, *Thesis*, Johns Hopkins University, 1922.

TABLE III, 6

ACTIVITY COEFFICIENTS AT 25 °C.

m	HCl	HBr	HI	H-ClO$_4$	H-NO$_3$	LiOH	LiCl	LiBr	LiI	Li-ClO$_4$	Li-NO$_3$	$\overline{\text{LiAc}}$
0·1	0·796	0·805	0·818	0·803	0·791	0·760	0·790	0·790	0·815	0·812	0·788	0·784
0·2	0·767	0·782	0·807	0·778	0·754	0·702	0·757	0·766	0·802	0·794	0·752	0·742
0·3	0·756	0·777	0·811	0·768	0·735	0·665	0·744	0·756	0·804	0·792	0·736	0·721
0·4	0·755	0·781	0·828	0·766	0·725	0·638	0·740	0·752	0·813	0·798	0·728	0·709
0·5	0·757	0·789	0·839	0·769	0·720	0·617	0·739	0·753	0·824	0·808	0·726	0·700
0·6	0·763	0·801	0·860	0·776	0·717	0·599	0·748	0·758	0·838	0·820	0·727	0·691
0·7	0·772	0·815	0·883	0·785	0·717	0·585	0·748	0·767	0·852	0·834	0·729	0·689
0·8	0·783	0·832	0·908	0·795	0·718	0·573	0·755	0·777	0·870	0·852	0·733	0·688
0·9	0·795	0·850	0·935	0·808	0·721	0·563	0·764	0·789	0·888	0·869	0·737	0·688
1·0	0·809	0·871	0·963	0·823	0·724	0·554	0·774	0·803	0·910	0·887	0·743	0·689
1·2	0·840	—	1·027	0·858	0·734	0·542	0·790	0·837	0·955	0·931	0·757	0·693
1·4	0·876	—	1·098	0·900	0·745	0·532	0·823	0·874	1·007	0·979	0·774	0·700
1·6	0·916	—	1·175	0·947	0·758	0·525	0·853	0·917	1·063	1·034	0·792	0·709
1·8	0·960	—	1·260	0·998	0·775	0·518	0·885	0·964	1·127	1·093	0·812	0·719
2·0	1·009	—	1·356	1·055	0·793	0·513	0·921	1·015	1·198	1·158	0·835	0·729
2·5	1·147	—	1·641	1·227	0·846	0·503	1·020	1·161	1·418	1·350	0·896	0·762
3·0	1·316	—	2·015	1·448	0·909	0·494	1·156	1·341	1·715	1·582	0·966	0·798
3·5	1·518	—	—	1·726	...	0·487	1·317	1·584	—	1·866	1·044	0·837
4·0	1·702	...	—	2·08	—	0·481	1·510	1·807	—	2·18	1·125	0·877
4·5	2·04	—	—	2·53	—	—	1·741	2·28	—	—	1·215	—
5·0	2·38	—	—	3·11	—	—	2·02	2·74	—	—	1·310	—
5·5	2·77	—	—	3·83	—	—	2·34	3·27	—	—	1·407	—
6·0	3·22	—	—	4·76	—	—	2·72	3·92	—	—	1·500	—
Ref.	16	19	20	41	42	22	10, 43	44, 45	10	46	47, 48	47

$\overline{\text{Ac}}$ = Acetate.

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TABLE III, 6 (*Continued*)

ACTIVITY COEFFICIENTS AT 25 °C.

m	LiTol	NaOH	NaF	NaCl	NaBr	NaI	Na-ClO$_3$	Na-ClO$_4$	Na-BrO$_3$	Na-NO$_3$	NaAc
0·1	0·772	0·700	0·765	0·778	0·782	0·787	0·772	0·775	0·758	0·762	0·791
0·2	0·723	0·727	0·710	0·735	0·741	0·751	0·720	0·729	0·696	0·703	0·757
0·3	0·695	0·708	0·676	0·710	0·719	0·735	0·688	0·701	0·657	0·666	0·744
0·4	0·674	0·697	0·651	0·698	0·704	0·727	0·664	0·683	0·628	0·638	0·737
0·5	0·659	0·690	0·632	0·681	0·697	0·723	0·645	0·668	0·605	0·617	0·735
0·6	0·647	0·685	0·616	0·673	0·692	0·723	0·630	0·656	0·585	0·599	0·736
0·7	0·638	0·681	0·603	0·667	0·689	0·724	0·617	0·648	0·569	0·583	0·740
0·8	0·630	0·679	0·592	0·662	0·687	0·727	0·606	0·641	0·554	0·570	0·745
0·9	0·623	0·678	0·582	0·659	0·687	0·731	0·597	0·635	0·541	0·558	0·752
1·0	0·617	0·678	0·573	0·657	0·687	0·736	0·589	0·629	0·528	0·548	0·757
1·2	0·605	0·681	—	0·654	0·692	0·747	0·575	0·622	0·507	0·530	0·769
1·4	0·595	0·686	—	0·655	0·699	0·763	0·563	0·616	0·489	0·514	0·789
1·6	0·586	0·692	—	0·657	0·700	0·780	0·553	0·613	0·473	0·501	0·809
1·8	0·575	0·700	—	0·662	0·718	0·799	0·545	0·611	0·461	0·489	0·829
2·0	0·568	0·709	—	0·668	0·731	0·820	0·538	0·600	0·450	0·478	0·851
2·5	0·558	0·743	—	0·688	0·768	0·888	0·525	0·609	0·426	0·455	0·914
3·0	0·556	0·784	—	0·714	0·812	0·963	0·515	0·611	—	0·437	0·982
3·5	0·559	0·835	—	0·746	0·865	1·053	0·508	0·617	—	0·422	1·057
4·0	0·566	0·903	—	0·783	0·929	—	—	0·626	—	0·408	—
4·5	0·575	0·985	—	0·826	—	—	—	0·637	—	0·396	—
5·0	—	1·077	—	0·874	—	—	—	0·640	—	0·386	—
5·5	—	1·181	—	0·928	—	—	—	0·662	—	0·378	—
6·0	—	1.290	—	0·986	—	—	—	0·677	—	0·371	—
Ref.	47	24,25 26,27	29	2	44, 40	44	50	46	51	47	47

$\overline{\text{Ac}}$ = Acetate. $\overline{\text{Tol}}$ = Toluenesulphonate.

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TABLE III, 6 (*Continued*)

ACTIVITY COEFFICIENTS AT 25 °C.

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m	$\overline{\text{NaTol}}$	Na-CNS	Na-H_2PO_4	KOH	KF	KCl	KBr	KI	$KClO_3$	K-BrO_3	KNO_3
0·1	0·765	0·787	0·744	0·798	0·775	0·770	0·772	0·778	0·749	0·745	0·739
0·2	0·709	0·750	0·675	0·760	0·727	0·718	0·722	0·733	0·681	0·674	0·663
0·3	0·674	0·731	0·629	0·742	0·700	0·688	0·698	0·707	0·635	0·625	0·614
0·4	0·648	0·720	0·593	0·734	0·682	0·666	0·678	0·680	0·599	0·585	0·576
0·5	0·627	0·715	0·565	0·732	0·670	0·649	0·657	0·670	0·568	0·552	0·545
0·6	0·609	0·712	0·539	0·738	0·661	0·637	0·646	0·667	0·541	—	0·519
0·7	0·593	0·710	0·517	0·730	0·654	0·626	0·636	0·660	0·518	—	0·496
0·8	0·579	0·710	0·499	0·742	0·650	0·618	0·629	0·654	—	—	0·476
0·9	0·566	0·711	0·483	0·740	0·646	0·610	0·622	0·649	—	—	0·459
1·0	0·554	0·712	0·468	0.750	0·645	0·604	0·617	0·645	—	—	0·443
1·2	0·532	0·716	0·442	0·776	0·643	0·593	0·608	0·640	—	—	0·414
1·4	0·511	0·723	0·420	0·800	0·644	0·586	0·602	0·637	—	—	0·390
1·6	0·493	0·730	0·401	0·827	0·647	0·580	0·598	0·636	—	—	0·369
1·8	0·476	0·737	0·385	0·856	0·652	0·576	0·595	0·636	—	—	0·350
2·0	0·460	0·744	0·371	0·888	0·658	0·573	0·593	0·637	—	—	0·333
2·5	0·427	0·779	0·343	0·974	0·678	0·569	0·593	0·644	—	—	0·297
3·0	0·402	0·804	0·320	1·081	0·705	0·569	0·595	0·652	—	—	0·269
3·5	0·383	0·854	0·305	1·215	0·738	0·572	0·600	0·662	—	—	0·246
4·0	0·368	0·897	0·293	1·352	0·779	0·577	0·608	0·673	—	—	—
4·5	—	—	0·283	1·53	—	0·583	0·616	0·683	—	—	—
5·0	—	—	0·276	1·72	—	—	0·626	—	—	—	—
5·5	—	—	0·270	1·95	—	—	—	—	—	—	—
6·0	—	—	0·265	2·20	—	—	—	—	—	—	—
Ref.	47	52	53	33, 34	20	2	44, 49	44, 54	51	55	47

<div align="center">

$\overline{\text{Tol}}$ = Toluensulphonate.

</div>

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TABLE III, 6 (*Continued*)

ACTIVITY COEFFICIENTS AT 25 °C.

m	$\overline{KAc}$	$\overline{KTol}$	K-CNS	KH$_2$-PO$_4$	RbCl	RbBr	RbI	Rb-NO$_3$	$\overline{RbAc}$	CsOH	CsCl	CsBr
0·1	0·796	0·702	0·769	0·731	0·764	0·763	0·762	0·734	0·796	0·705	0·756	0·754
0·2	0·766	0·702	0·716	0·653	0·709	0·706	0·705	0·658	0·707	0·761	0·694	0·694
0·3	0·754	0·602	0·685	0·602	0·675	0·673	0·671	0·606	0·756	0·744	0·656	0·654
0·4	0·750	0·632	0·663	0·561	0·652	0·650	0·647	0·565	0·753	0·739	0·628	0·626
0·5	0·751	0·605	0·646	0·529	0·634	0·632	0·629	0·534	0·755	0·739	0·606	0·603
0·6	0·754	0·582	0·633	0·501	0·620	0·617	0·614	0·508	0·759	0·742	0·589	0·586
0·7	0·759	0·500	0·623	0·477	0·608	0·605	0·602	0·485	0·766	0·748	0·575	0·571
0·8	0·766	0·541	0·614	0·456	0·599	0·595	0·591	0·465	0·778	0·754	0·563	0·558
0·9	0·774	0·523	0·606	0·438	0·590	0·586	0·583	0·446	0·782	0·762	0·553	0·547
1·0	0·783	0·506	0·599	0·421	0·583	0·578	0·575	0·430	0·792	0·771	0·544	0·538
1·2	0·803	0·476	0·587	0·393	0·572	0·565	0·562	0·402	0·815	—	0·529	0·523
1·4	0·827	0·448	0·577	0·369	0·563	0·556	0·551	0·377	0·840	—	0·518	0·510
1·6	0·854	0·424	0·569	0·348	0·556	0·547	0·544	0·356	0·860	—	0·509	0·500
1·8	0·881	0·404	0·562	0·332	0·551	0·541	0·537	0·338	0·900	—	0·501	0·493
2·0	0·910	0·386	0·556	—	0·546	0·536	0·533	0·321	0·933	—	0·495	0·486
2·5	0·995	0·347	0·540	—	0·539	0·526	0·524	0·285	1·023	—	0·484	0·474
3·0	1·086	0·317	0·538	—	0·536	0·520	0·518	0·257	1·126	—	0·478	0·465
3·5	1·181	0·292	0·533	—	0·536	0·516	0·516	0·234	1·240	—	0·474	0·460
4·0	—	—	0·529	—	0·538	0·514	0·515	0·216	—	—	0·473	0·457
4·5	—	—	0·526	—	0·541	0·514	0·510	0·200	—	—	0·473	0·455
5·0	—	—	0·524	—	0·546	0·515	0·517	—	—	—	0·474	0·453
5·5	—	—	—	—	—	—	—	—	—	—	—	—
6·0	—	—	—	—	—	—	—	—	—	—	—	—
Ref.	47	47	52	53	10, 56	44, 56	44, 56	47, 56	47, 56	36	10, 36	44, 56

$\overline{Ac}$ = Acetate. $\overline{Tol}$ = Toluenesulphonate.

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TABLE III, 6 (*Continued*)

ACTIVITY COEFFICIENTS AT 25 °C.

m	CsI	CsNO$_3$	Cs$\overline{\text{Ac}}$	AgNO$_3$	TlClO$_4$	TlNO$_3$	Tl$\overline{\text{Ac}}$	CuSO$_4$	MgSO$_4$
0·1	0·754	0·733	0·799	0·784	0·730	0·702	0·750	(0·150)	(0·150)
0·2	0·692	0·655	0·771	0·657	0·652	0·606	0·686	0·104	0·108
0·3	0·651	0·602	0·761	0·606	0·599	0·545	0·644	0·083	0·088
0·4	0·621	0·561	0·750	0·567	0·559	0·500	0·614	0·071	0·076
0·5	0·599	0·528	0·762	0·586	0·527	—·—	0·589	0·062	0·068
0·6	0·581	0·501	0·768	0·509	—	—··	0·570	0·056	0·062
0·7	0·567	0·478	0·776	0·485	—	—	0·553	0·052	0·057
0·8	0·554	0·458	0·783	0·464	—	—	0·539	0·048	0·054
0·9	0·543	0·439	0·792	0·446	—	—	0·526	0·045	0·051
1·0	0·533	0·422	0·802	0·429	—	—	0·515	0·043	0·049
1·2	0·516	0·393	0·826	0·399	—··	—	0·496	0·039	0·045
1·4	0·501	0·368	0·858	0·374	—	—	0·480	0·037	0·044
1·6	0·489	—	0·883	0.352	—	·—·	0·466	—	0·042
1·8	0·479	—	0·916	0.333	—	—	0·454	—	0·042
2·0	0·470	·—	0·950	0.316	—··	—	0·444	—	0·042
2·5	0·450	—	1·041	0·280	—·—	—	0·422	—	0·044
3·0	0·434	—··	1·145	0·252	—	—	0·405	—·	0·049
3·5	—	—	1·263	0·229	·—·	—	0·389	—	—
4·0	—··	—	——	0·210	·—··	—	0·376	—	—·—
4·5	··	—··	—	0·194	·····	—	0·364	—	—
5·0	—	··—	—··	0·181	—	—	0·354	—··	—
5·5	—	—	—	0·169	—···	—	0·344	—··	—
6·0	—··	—	—·	0·150	—	—	0·335	—	—
Ref.	44, 56	47, 56	47, 56	57	56	56	56	58	58

$\overline{\text{Ac}}$ = Acetate.

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TABLE III, 6 *(Continued)*

ACTIVITY COEFFICIENTS AT 25° C.

m	Zn-SO$_4$	Cd-SO$_4$	Mn-SO$_4$	Ni-SO$_4$	AlCl$_3$	ScCl$_3$	CrCl$_3$	YCl$_3$	LaCl$_3$	CeCl$_3$	PrCl$_3$	NdCl$_3$
0·1	(·150)	(·150)	(·150)	(·150)	(·337)	(·320)	(·331)	(·314)	(·314)	(·309)	(·311)	(·310)
0·2	0·104	0·102	0·106	0·105	0·305	0·288	0·298	0·278	0·274	0·273	0·278	0·272
0·3	0·083	0·082	0·085	0·084	0·302	0·282	0·294	0·269	0·263	0·261	0·260	0·261
0·4	0·071	0·069	0·073	0·071	0·313	0·287	0·300	0·271	0·261	0·260	0·258	0·259
0·5	0·063	0·061	0·064	0·063	0·331	0·298	0·314	0·278	0·266	0·264	0·262	0·264
0·6	0·057	0·055	0·058	0·056	0·356	0·316	0·335	0·291	0·274	0·272	0·268	0·272
0·7	0·052	0·050	0·053	0·052	0·388	0·339	0·362	0·307	0·285	0·286	0·281	0·284
0·8	0·048	0·046	0·049	0·047	0·429	0·369	0·397	0·329	0·302	0·302	0·297	0·301
0·9	0·046	0·043	0·046	0·044	0·479	0·403	0·436	0·355	0·321	0·320	0·316	0·321
1·0	0·043	0·041	0·044	0·042	0·539	0·443	0·481	0·385	0·342	0·342	0·338	0·344
1·2	0·040	0·038	0·040	0·039	0·701	0·544	0·584	0·462	0·398	0·395	0·395	0·403
1·4	0·038	0·035	0·038	0·036	0·936	0·677	—	0·566	0·470	0·469	0·467	0·480
1·6	0·036	0·034	0·037	0·035	1·284	0·858	—	0·701	0·561	0·559	0·558	0·577
1·8	0·035	0·032	0·036	0·034	1·810	1·089	—	0·884	0·677	0·684	0·675	0·704
2·0	0·035	0·032	0·035	0·034	—	—	—	1·186	0·825	0·847	0·825	0·807
2·5	0·037	0·032	0·035	0·035	—	—	—	—	—	—	—	—
3·0	0·041	0·033	0·038	—	—	—	—	—	—	—	—	—
3·5	0·043	0·035	0·042	—	—	—	—	—	—	—	—	—
4·0	—	—	0·048	—	—	—	—	—	—	—	—	—
Ref.	58	58	58	58	59	59	60	59	59, 61	59	59	59

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TABLE III, 6 *(Continued)*

ACTIVITY COEFFICIENTS AT 25 °C.

m	$SmCl_3$	$EuCl_3$	$Cr(NO_3)_3$	$K_3Fe(CN)_6$	$K_4Fe(CN)_6$	$Al_2(SO_4)_3$	$Cr_2(SO_4)_3$	$Th(NO_3)_4$
0·1	(0·314)	(0·318)	(0·319)	(0·268)	(0·189)	(0·0850)	(0·0458)	(0·279)
0·2	0·278	0·282	0·285	0·212	0·100	0·0225	0·0300	0·225
0·3	0·267	0·270	0·279	0·184	0·081	0·0176	0·0238	0·203
0·4	0·266	0·270	0·281	0·167	0·070	0·0153	0·0207	0·192
0·5	0·271	0·276	0·291	0·155	0·062	0·0143	0·0190	0·189
0·6	0·280	0·286	0·304	0·146	0·056	0·0140	0·0182	0·188
0·7	0·296	0·303	0·322	0·140	0·052	0·0142	0·0181	0·191
0·8	0·314	0·322	0·344	0·135	0·048	0·0149	0·0185	0·195
0·9	0·336	0·345	0·371	0·131	0·046	0·0159	0·0194	0·201
1·0	0·362	0·371	0·401	0·128	—	0·0175	0·0208	0·207
1·2	0·424	0·436	0·474	0·124	—	—	0·0250	0·224
1·4	0·509	0·525	0·565	0·122	—	—	—	0·246
1·6	0·616	0·641	—	—	—	—	—	0·269
1·8	0·756	0·792	—	—	—	—	—	0·296
2·0	0·940	0·965	—	—	—	—	—	0·320
2·5	—	—	—	—	—	—	—	0·405
3·0	—	—	—	—	—	—	—	0·486
3·5	—	—	—	—	—	—	—	0·568
4·0	—	—	—	—	—	—	—	0·647
4·5	—	—	—	—	—	—	—	0·722
5·0	—	—	—	—	—	—	—	0·791
Ref.	62	62	60	63	56	56	60	63

[61] R. A. ROBINSON, *Trans. Faraday Soc.*, 1939, **35**, 1229.

[62] C. M. MASON, *J. Am. Chem. Soc.*, 1941, **63**, 220.

[63] R. A. ROBINSON and B. J. LEVIEN, *Trans. Roy. Soc. N.Z.*, 1946, **76**, 295.

TABLE III, 7

OSMOTIC AND ACTIVITY COEFFICIENTS AT HIGH CONCENTRATIONS $(m > 6)$

	HCl		HClO$_3$		LiCl		LiBr		LiNO$_3$	
m	f_0	$f_\pm$	f_0	$f_\pm$	f_0	$f_\pm$	f_0	$f_\pm$	f_0	$f_\pm$
7	2·008	4·37	2·365	7·44	1·965	3·71	2·200	5·76	1·485	1·728
8	2·163	5·90	2·620	11·83	2·143	5.10	2·432	8·01	1·541	1·952
9	2·315	7·94	2·901	19·11	2·310	6.96	2.656	12·92	1·591	2·19
10	2·444	10·44	3·107	30·9	2·464	9·40	2·902	19·92	1·638	2·44
11	2·559	13·51	3·433	50·1	2·607	12·55	3·150	31·0	1·668	2·69
12	2·663	17·25	3·688	80·8	2·730	16·41	3·350	46·3	1·700	2·95
13	2·760	21·8	3·935	129·5	2·830	20·9	3·581	70·6	1·727	3·20
14	2·853	27·3	4·166	205·0	2·915	26·2	3·776	104·7	---	—
15	2·944	34·1	4·393	322·0	2·978	31·9	3·912	146·0	—	---
16	3·033	42·4	4·608	500·0	3·023	37·0	4·025	198·0	---	—
17	---	---	—	—	3·044	43·8	4·110	260·0	---	—
18	—	—	—	—	3·057	49·9	4·173	331·0	---	—
19	—	---	—	---	3·066	56·3	4·216	411·0	—	---
20	—	—	—	—	3·063	62·4	4·217	485·0	—	—

	KOH		NaOH		AgNO$_3$	
m	f_0	$f_\pm$	f_0	$f_\pm$	f_0	$f_\pm$
7	1·81	2·88	1·567	1·603	0·426	0·142
8	1·96	3·77	1·707	2·01	0·408	0·129
9	2·09	4·86	1·853	2·55	0·393	0·118
10	2·22	6·22	1·993	3·23	0·378	0·109
11	2·36	8·10	2·131	4·10	0·371	0·102
12	2·50	10·5	2·262	5·19	0·363	0·096
13	2·60	13·2	2·382	6·50	0·350	0·090
14	2·66	15·8	2·488	8·04	---	—
15	2·76	19·0	2·574	9·74	—	—
16	2·87	24·6	2·643	11·58	—	—
17	—	—	2·694	13·47	—	—
18	—	—	2·730	15·41	—	—
19	—	—	2·756	17·38	—	—
20	—	—	2·772	19·33	—	—

SODIUM HYDROXIDE

m	21·0	22·0	23·0	24·0	25·0	26·0	27·0	28·0	29·0
f_0	2·780	2·780	2·773	2·764	2·749	2·731	2·712	2·693	2·678
$f_\pm$	21·3	23·1	24·6	26·5	28·0	29·5	30·9	32·2	33·7

TABLE III, 8

MEAN ACTIVITY COEFFICIENT OF POTASSIUM CHLORIDE IN AQUEOUS SOLUTION

molality m	0°	5°	10°	15°	20°	25°	30°	35°	40°
0·1	0·768	0·769	0·769	0·769	0·770	0·769	0·768	0·767	0·765
0·2	·717	·718	·718	·719	·718	·719	·718	·717	·715
0·3	·688	·685	·687	·687	·688	·688	·687	·685	·682
0·5	·642	·646	·648	·650	·651	·651	·651	·648	·646
0·7	·618	·619	·623	·624	·627	·628	·629	·627	·620
1·0	·588	·595	·598	·601	·604	·606	·604	·604	·603
1·5	·563	·570	·576	·579	·582	·585	·585	·585	·585
2·0	·547	·554	·562	·568	·573	·576	·578	·579	·578
2·5	·540	·549	·556	·562	·568	·572	·574	·575	·575
3·0	·539	·549	·556	·562	·567	·571	·573	·574	·573
3·5	·540	·550	·558	·565	·571	·574	·577	·578	·578
4·0	—	—	·563	·569	·574	·579	·582	·584	·585

H. S. HARNED and M. A. COOK, *J. Am. Chem. Soc.*, 1937, 59, 1290.

TABLE III, 8a

MEAN ACTIVITY COEFFICIENT OF SODIUM BROMIDE IN AQUEOUS SOLUTION

molality m	0°	5°	10°	15°	20°	25°	30°	35°	40°
0·1	(0·784)	(0·784)	(0·784)	(0·783)	(0·783)	(0·782)	(0·781)	(0·779)	(0·777
0·2	·738	·739	·741	·740	·741	·740	·739	·737	·734
0·3	·713	·716	·718	·720	·718	·718	·717	·715	·712
0·5	·685	·689	·693	·693	·695	·695	·694	·692	·689
0·7	·670	·675	·681	·684	·683	·687	·686	·685	·685
1·0	·659	·667	·675	·680	·684	·686	·687	·686	·686
1·5	·664	·673	·686	·693	·699	·703	·706	·708	·707
2·0	·679	·693	·708	·719	·727	·734	·739	·741	·743
2·5	·708	·727	·745	·733	·769	·778	·784	·789	·791
3·0	·745	·766	·787	·802	·815	·826	·834	·839	·842
3·5	·787	·811	·834	·852	·866	·878	·887	·893	·896
4·0	·832	·858	·885	·905	·921	·934	·945	·951	·954

Accuracy: Agreement with SMITH [1] and SPENCER [2] to ±0·001.

H. S. HARNED and C. C. CRAWFORD, *ibid.*, 1937, 59, 1903.

[1] R. P. SMITH, *ibid.*, 1933, 55, 3279.
[2] H. M. SPENCER, *ibid.*, 1932, 54, 4490.

TABLE III, 9

MEAN ACTIVITY COEFFICIENT OF POTASSIUM HYDROXIDE IN AQUEOUS SOLUTION

molality m	0°	5°	10°	15°	20°	25°	30°	35°
0·05	(0·829)	(0·828)	(0·828)	(0·827)	(0·825)	(0·824)	(0·823)	(0·822)
0·1	·795	·796	·798	·798	·798	·798	·796	·798
0·15	·778	·778	·778	·777	·776	·774	·773	·771
0·25	·758	·757	·759	·758	·757	·757	·753	·751
0·35	·738	·740	·740	·739	·739	·739	·736	·733
0·5	·737	·736	·735	·734	·732	·728	·725	·725
0·75	·742	·742	·743	·743	·741	·740	·740	·736
1·0	·755	·756	·758	·757	·756	·756	·755	·752
1·5	·800	·812	·815	·815	·814	·814	·812	·809
2·0	·889	·886	·890	·890	·889	·888	·884	·879
2·5	·974	·978	·981	·982	·980	·974	·972	·965
3·0	1·088	1·091	1·094	1·003	1·087	1·081	1·072	1·065
3·5	1·210	1·229	1·231	1·220	1·219	1·215	1·199	1·195
4·0	1·391	1·395	1·380	1·381	1·361	1·352	1·384	1·314

Accuracy: Observed $f_\pm$ and calculated values agree to $\pm 0.25\%$
H. S. HARNED and M. A. COOK, *J. Am. Chem. Soc.*, 1937, 59, 496.

TABLE III, 10

MEAN ACTIVITY COEFFICIENT OF SODIUM HYDROXIDE IN AQUEOUS SOLUTION

molality m [1]	0°	5°	10°	15°	20°	25°	30°	35°
0·05	0·820	0·821	0·820	0·820	0·819	0·818	0·818	0·810
0·1	·767	·768	·768	·767	·766	·766	·765	·764
0·25	·713	·715	·716	·717	·714	·713	·712	·712
0·5	·648	·688	·090	·692	·693	·693	·693	·694
1·0	·660	·668	·672	·676	·678	·679	·680	·678
1·5	·661	·669	·673	·681	·682	·688	·685	·683

Accuracy: [1] $\pm 0.25\%$

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[1] 0·05 to 1·5M, H. S. HARNED and J. C. HECKER, *J. Am. Chem. Soc.*, 1933, 55, 4838.

TABLE III, 10 (*Continued*)

molality m (¹)	0°	10°	20°	30°	40°	50°	60°	70°
1·5	0·657	0·679	0·685	0·688	0·684	0·674	0·657	0·635
2·0	·682	·702	·709	·712	·707	·696	·677	·652
3·0	·763	·766	·769	·761	·753	·767	·742	·711
4·0	·900	·920	·916	·911	·895	·872	·839	·800
5·0	1·100	1·109	1·098	1·081	1·053	1·017	·971	·822
6·0	1·39	1·40	1·35	1·32	1·27	1·21	1·14	1·07
8·0	2·35	2·31	2·17	2·06	1·93	1·78	1·63	1·48
10·0	4·12	4·00	3·61	3·31	3·00	2·67	2·34	2·03
12·0	7·16	6·67	5·80	5·11	4·43	3·79	3·19	2·65
14·0	11·4	10·00	8·68	7·43	6·26	5·20	4·26	3·43
17·0	22·5	19·0	15·82	13·00	10·52	8·39	6·60	5·11

¹ 1·5 to 17M, G. Åkerlöf and G. Kegeles, *J. Am. Chem. Soc.*, 1940, 62, 620.

TABLE III, 11

ACTIVITIES OF WATER IN ELECTROLYTE SOLUTIONS AT 25 °C.

From e.m.f. data for the cell Pt H₂ | H₂SO₄ | PbSO₄ | PbO₂ Pt accurate to ± 0.0005 v.

Aq. KCl solution			
c (g.equiv./l.)	—log. a_w	c (g.equiv./l.)	—log. a_w
0·05	0·000733	1·0	0·014061
0·1	0·001450	2·0	0·02860
0·2	0·002863	3·0	0·04393
0·3	0·004256	4·0	0·06042
0·5	0·002051		

Aq. H₂SO₄ solution			
c	a_w	c	a_w
0·01	0·99951	2·0	0·9136
0·02	0·99912	5·0	0·6981
0·05	0·99801	7·0	0·5453
0·1	0·09628	11·0	0·3171
0·2	0·99278	15·0	0·1763
0·5	0·98205	17·0	0·1289
1·0	0·96217		

R. H. Stokes, *J. Am. Chem. Soc.*, 1945, 67, 1086.

H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, 1935, 57, 27.

S. Shankman and A. R. Gordon, *J. Am. Chem. Soc.*, 1939, 61, 2370.

From observed electromotive forces. Results at concentrations less than $m = 0.002$ are based on the data of H. S. HARNED and R. W. EHLERS, (*J. Am. Chem. Soc.*, made a careful study of the hydrogen silver-silver chloride cell containing were made for the solubility of

molality m	0°	5°	10°	15°	20°	25°
0·0001	(0·9890)	(0·9886)	(0·9890)	(0·9890)	(0·9892)	(0.9891)
·0002	(·9848)	(·9847)	(·9846)	(·9844)	(·9844)	(·9842)
·0005	(·9756)	(·9756)	(·9756)	(·9757)	(·9759)	(·9752)
·001	(·9668)	(·9662)	(·9666)	(·9661)	(·9661)	(·9656)
·002	·9541	·9539	·9544	·9580	·9527	·9521
·005	·9303	·9300	·9300	·9207	·9294	·9285
·01	·9065	·9056	·9055	·9055	·9052	·9048
·02	·8774	·8708	·8773	·8770	·8768	·8755
·05	·8346	·8344	·8338	·8329	·8317	·8304
·1	·8027	·8023	·8016	·8000	·7985	·7964
·2	·7756	·7756	·7740	·7717	·7694	·7667
·5	·7761	·7730	·7694	·7658	·7616	·7571
1·0	·8419	·8363	·8295	·8229	·8102	·8090
1·5	·9452	·9365	·9270	·9154	·9005	·8962
2·0	1·078	1·068	1·053	1·039	1·024	1·009
3·0	1·452	1·427	1·401	1·373	1·345	1·316
4·0	2·006	1·960	1·911	1·862	1·812	1·762

See also Table III, 7.
Accuracy: ±0·06%

molality m	0°	5°	10°	15°	20°	25°
0·001	0·967	0·967	0·967	0·966	0·966	0·966
·005	·932	·932	·932	·930	·930	·930
·01	·910	·910	·909	·908	·907	·906
·02	·883	·883	·883	·882	·879	·879
·05	·843	·843	·843	·842	·838	·838
·1	·812	·812	·811	·808	·807	·805
·2	·793	·791	·790	·787	·785	·782
·5	·806	·803	·800	·797	·793	·790
1·0	·900	·894	·889	·888	·877	·871

Accuracy: Agreement between observed and calculated values to within ±0·25%, experimental accuracy: probably ±0·1%.

III, 11

HYDROCHLORIC ACID IN WATER

were obtained from plots used for extrapolation (values in brackets). These values
1933, 55, 2179). N. J. ANDERSON, *Dissertation*, University of Chicago (1934), has
hydrochloric acid at concentrations between 0·00002 and 0·003m. Corrections
silver chloride and for other effects.

30°	35°	40°	45°	50°	55°	60°
(0·9890)	(0·9886)	(0·9885)	(0·9883)	(0·9879)	(0·9879)	(0·9879)
(·9835)	(·9833)	(·9833)	(·9835)	(·9831)	(·9833)	(·9831)
(·9747)	(·9745)	(·9741)	(·9741)	(·9738)	(·9735)	(·9734)
(·9650)	(·9647)	(·9643)	(·9644)	(·9639)	(·9636)	(·9632)
·9515	·9513	·9505	·9504	·9500	·9497	·9491
·9275	·9268	·9265	·9261	·9250	·9240	·9235
·9034	·9025	·9016	·9008	·9000	·8990	·8987
·8741	·8731	·8715	·8704	·8690	·8680	·8666
·8285	·8265	·8246	·8232	·8211	·8195	·8168
·7940	·7918	·7891	·7872	·7850	·7829	·7813
·7630	·7604	·7569	·7538	·7508	·7474	·7437
·7526	·7477	·7432	·7387	·7344	·7292	·7237
·8018	·7942	·7865	·7790	·7697	·7628	·7541
·8849	·8740	·8601	·8517	·8404	·8276	·8178
·9029	·9755	·9602	·9481	·9327	·9186	·9072
—	—	—	—	—	—	—
—	—	—	—	—	—	—

III, 13

HYDROBROMIC ACID IN AQUEOUS SOLUTION [1]

30°	35°	40°	45°	50°	55°	60°
0·966	0·965	0·964	0·964	0·964	0·963	0·963
·929	·928	·928	·927	·926	·924	·924
·906	·905	·904	·904	·902	·900	·898
·879	·878	·877	·875	·873	·871	·869
·837	·834	·833	·831	·830	·827	·826
·804	·802	·800	·797	·795	·791	·788
·780	·777	·774	·772	·769	·765	·758
·784	·781	·776	·772	·767	·764	·760
·864	·856	·850	·844	·838	·831	·828

[1] H. S. HARNED, A. S. KESTON and J. G. DONELSON, *J. Am. Chem. Soc.*, 1937,
58, 989.

TABLE III, 14

MEAN ACTIVITY COEFFICIENT OF HYDROCHLORIC ACID IN ORGANIC SOLVENTS AND
ORGANIC SOLVENT-WATER MIXTURES

N_2 = mol. fraction of organic solvent. (Figures in brackets refer to references)

I. Methanol

molality of HCl m	$N_2 = 0.0588$ [1]			$N_2 = 0.1233$ [1]		
	0°	25°	40°	0°	25°	40°
0·001	0·964	0·962	0·961	0·961	0·959	0·957
·002	·951	·948	·940	·946	·943	·941
·005	·926	·922	·919	·919	·915	·912
·01	·901	·897	·893	·893	·888	·884
·02	·872	·866	·861	·862	·856	·850
·05	·825	·819	·812	·814	·806	·798
·1	·790	·780	·772	·771	·762	·751
·2	·762	·747	·736	·741	·727	·715
·5	·754	·737	·718	·726	·703	·693
1·0	·800	·783	·756	·772	·747	·722
1·5	·898	·861	·827	·855	·814	·781
2·0	1·020	·966	·917	·965	·911	·860

$N_2 = 1$ [2]

molality of HCl m	25°	m	25°	m	25°
0·00236	0·826	0·01444	0·658	0·0733	0·470
·002683	·817	·01722	·638	·0751	·468
·002980	·809	·01986	·621	·0947	·443
·003161	·804	·02303	·601	·1155	·423
·00404	·766	·02549	·592	·4302	·325
·00542	·758	·04261	·582	·5574	·322
·00711	·732	·04856	·530	—	—
·00966	·699	·05312	·507	—	—

[1] H. S. HARNED and C. H. THOMAS, *J. Am. Chem. Soc.*, 1936, **58**, 761.

[2] G. NONHEBEL and H. HARTLEY, *Phil. Mag.*, 1928, **50**, (6), 298, 729.

TABLE III, 14 (*Continued*)

II. Ethanol

$N_1 = 0.0417$ [3]		$N_1 = 0.0891$ [3]		$N_1 = 0.5$ [4, 5]		$N_1 = 1$ [4, 5]	
m	25°	m	25°	m	25°	m	25°
0·00631	0·914	0·00470	0·915	0·005	0·815	0·005	0·728
·00758	·907	·00787	·894	·01	·757	·01	·632
·01088	·891	·01015	·883	·02	·676	·02	·544
·01987	·864	·01988	·850	·05	·586	·0249	·514
·04210	·824	·04150	·809	·1	·521	·0423	·445
·05100	·814	·05166	·794	·2	·471	·05	·426
·07085	·795	·07123	·775	·5	·432	·1	·352
·0800	·788	·0816	·770	1·0	·449	·1242	·327
·0885	·783	·0924	·761	1·5	·510	·1762	·300
·1091	·778	·1042	·751	2·0	·582	·2	·286
·1090	·744	·3088	·690	2·5	·607	·4437	·218
·2909	·731	·4751	·698	—	—	1·0	·177
·5050	·730	·7300	·709	—	—	1·050	·168
·7014	·743	1·0216	·741	—	—	1·481	·159
·9946	·770	1·549	·819	—	—	3·62	·150
1·499	·856	2·079	·930	—	—	—	—
1·904	·954	—	—	—	—	—	—

III. Isopropanol [3]

$N_1 = 0.0323$

m	25°	m	25°	m	25°
0·001862	0·948	0·03558	0·830	0·2990	0·726
·004019	·927	·04855	·813	·4451	·723
·006856	·911	·06685	·795	·6993	·737
·008616	·899	·07947	·785	·8863	·757
·00892	·898	·1119	·766	1·0	·770
·02089	·858	·1921	·740	—	—

[3] H. S. HARNED and C. CALMON, *J. Am. Chem. Soc.*, 1939, **61**, 1491.

[4] H. S. HARNED and M. H. FLEYSHER, *ibid.*, 1925, **47**, 82.

[5] W. W. LUCASSE, *Z. physik. Chem.*, 1926, **121**, 254.

TABLE III, 14 (*Continued*)

IV. Glycerol ([2])

m	$N_3 = 0.01$ 25°	$N_3 = 0.05$ 25°	m	$N_3 = 0.01$ 25°	$N_3 = 0.05$ 25°
0·002	0·951	—	0·5	0·755	0·787
·005	·924	0·898	0·7	·772	·760
·01	·902	·885	1·0	·810	·801
·02	·873	·858	1·5	·901	·901
·05	·826	·810	2·0	1·019	1·030
·1	·798	·775	2·5	1·161	1·190
·2	·764	·744	3·0	1·345	1·385
·28	·756	·738	4·0	1·792	1·914
·38	·753	·738	—	—	—

Accuracy: Agreement between observed and calculated $f_\pm$ is $\pm 0.001 - 0.002$.
Accuracy of basic e.m.f. data is ± 0.05 mv.

TABLE III, 15

ACTIVITY COEFFICIENTS OF SALTS IN ANHYDROUS AMMONIA AT —50 °C.

$f_\pm (NH_4NO_3)$		$f_\pm (NH_4Cl)$	
c mol/l.	$f_\pm$	c mol/l.	$f_\pm$
0·0001	0·953	0·005	0·423
0·0002	0·935	0·01	0·341
0·0005	0·883	0·02	0·266
0·001	0·824	0·05	0·188
0·005	0·578	0·1	0·143
0·01	0·466	0·2	0·106
0·05	0·282	0·5	0·070
0·1	0·216		
0·5	0·122		
1·0	0·104		

V. A. PLESKOV and A. M. MONOSSOHN, *Acta Physicochim.*, *U.R.S.S.*, 1934, 1, 718.

TABLE III, 16

MEAN ACTIVITY COEFFICIENTS OF HYDROCHLORIC ACID IN DIOXANE-WATER MIXTURES

$(X = \text{wt.\%} \text{ DIOXANE})$

m	0°	10°	20°	25°	30°	40°	50°
			$X = 20$				
0·005	0·902	0·900	0·898	0·896	0·895	0·892	0·889
·007	·889	·886	·883	·880	·880	·876	·871
·01	·872	·869	·865	·862	·861	·857	·851
·02	·835	·830	·825	·821	·820	·814	·808
·03	·811	·805	·800	·796	·795	·788	·781
·05	·780	·774	·768	·763	·762	·755	·748
·07	·750	·753	·746	·740	·740	·732	·725
·1	·736	·729	·722	·720	·716	·708	·701
·2	·696	·688	·681	·676	·673	·665	·656
·3	·682	·675	·667	·661	·658	·649	·639
·5	·684	·675	·666	·660	·650	·646	·633
·7	·649	·690	·679	·672	·667	·655	·641
1·0	·736	·725	·712	·704	·698	·683	·666
1·5	·830	·815	·797	·786	·777	·755	·732
2·0	·959	·938	·913	·898	·885	·855	·828
3·0	1·337	1·293	1·245	1·219	1·195	1·141	1·085
			$X = 45$				
0·003	0·849	0·846	0·844	0·842	0·839	0·834	0·828
·005	·824	·817	·811	·808	·803	·795	·786
·007	·802	·793	·786	·782	·777	·767	·757
·01	·776	·766	·758	·753	·747	·737	·725
·02	·720	·707	·697	·692	·686	·673	·660
·03	·688	·671	·661	·654	·649	·635	·622
·05	·637	·624	·613	·607	·600	·586	·573
·07	·605	·593	·583	·577	·570	·557	·545
·1	·579	·566	·553	·547	·540	·525	·512
·2	·529	·514	·503	·496	·488	·474	·459
·3	·511	·496	·484	·476	·466	·453	·438
·5	·503	·487	·473	·465	·456	·440	·423
·7	·513	·495	·480	·471	·461	·448	·424
1·0	·547	·526	·508	·497	·485	·463	·442
1·5	·640	·612	·585	·570	·555	·524	·490
2·0	·778	·738	·695	·676	·655	·614	·575
3·0	1·191	1·112	1·037	1·001	·962	·887	·818

TABLE III, 10 (*Continued*)

m	0°	10°	20°	25°	30°	40°	50°
			$X = 70$				
0·001	0·719	0·718	0·705	0·700	0·696	0·686	0·675
·0015	·672	·665	·650	·651	·647	·636	·624
·002	·641	·633	·628	·618	·618	·601	·589
·003	·589	·582	·573	·568	·563	·552	·540
·005	·530	·521	·510	·505	·490	·487	·478
·007	·488	·479	·468	·462	·457	·444	·431
·01	·446	·436	·425	·418	·413	·401	·388
·02	·369	·359	·348	·342	·336	·324	·312
·03	·328	·318	·308	·303	·297	·286	·275
·05	·283	·274	·264	·258	·253	·243	·232
·07	·259	·249	·239	·234	·229	·219	·208
·1	·236	·226	·217	·212	·207	·197	·188
·2	·204	·194	·185	·180	·175	·165	·156
·3	·193	·182	·173	·168	·163	·154	·144
·5	·191	·179	·169	·163	·158	·147	·137
·7	·200	·187	·175	·168	·162	·150	·139
1·0	·227	·211	·195	·187	·179	·165	·151
1·5	·303	·277	·252	·240	·228	·207	·187

m	5°	15°	25°	35°	45°
			$X = 82$		
0·001	0·4242	0·4129	0·3979	0·3795	0·3502
·0015	·3725	·3627	·3488	·3318	·3129
·002	·3369	·3277	·3147	·2990	·2810
·003	·2862	·2781	·2682	·2553	·2378
·005	·2319	·2267	·2181	·2062	·1916
·007	·2019	·1977	·1900	·1791	·1654
·01	·1744	·1707	·1629	·1529	·1412
·025	·1472	·1440	·1371	·1282	·1176
·02	·1311	·1274	·1213	·1131	·1035
·03	·1112	·1076	·1020	·0946	·0869
·05	·0912	·0876	·0826	·0766	·0698
·07	·0780	·0756	·0713	·0659	·0596
·1	·0701	·0675	·0634	·0582	·0525
·15	·0627	·0597	·0500	·0518	·0460
·2	·0589	·0500	·0521	·0476	·0425
·3	·0563	·0532	·0490	·0443	·0392
·5	·0595	·0554	·0504	·0445	·0886

H. S. HARNED and J. O. MORRISON, *Am. J. Sci.*, 1937, 33, 161; *J. Am. Chem. Soc.*, 1936, 58, 1008.

TABLE III, 17

ACTIVITY COEFFICIENTS OF LEAD CHLORIDE IN ETHYLENE GLYCOL-WATER MIXTURES AT 25 °C.

$I_{(m)}$	100% H_2O	78·25% H_2O	57·43% H_2O	37·56% H_2O	19·30% H_2O	0% H_2O
0·001	0·912	0·910	0·895	0·866	0·828	0·798
0·003	0·847	0·844	0·820	0·775	0·715	0·677
0·006	0·791	0·786	0·755	0·701	0·637	0·591
0·008	0·764	0·758	0·724	0·666	0·594	0·553
0·01	0·740	0·732	0·697	0·635	0·562	0·520
0·03	0·604	0·593	0·551	0·483	0·407	0·364
0·06	0·505	0·494	0·450	0·385	0·316	0·275
0·08	0·464	0·452	0·410	0·348	0·282	0·241
0·1146	0·413	0·402	0·363	0·305	0·243	0·202
0·1307	0·385	0·372	0·336	0·283	0·226	0·182
0·2	0·335	0·320	0·290	0·243	0·196	0·144
0·4	—	0·236	0·217	0·193	0·166	—
0·8	—	0·166	0.160	0.148	—	—

Solvent composition is given as wt.% H_2O.

ACTIVITY COEFFICIENTS OF THALLOUS CHLORIDE IN GLYCOL-WATER MIXTURES AT 25 °C.

$I_{(m)}$	0% Glycol	20% Glycol	40% Glycol	60% Glycol	80% Glycol	100% Glycol
0·001	0·957	0·953	0·950	0·917	0·890	0·827
0·004	0·921	0·911	0·895	0·848	0·807	0·721
0·007	0·897	0·880	0·861	0·808	0·763	0·668
0·010	0·881	0·862	0·833	0·780	0·732	0·635
0·040	0·777	0·739	0·695	0·642	0·605	0·503
0·100	0·680	0·615	0·576	0·544	0·518	0·427
0·300	0·529	0·470	0·441	0·430	—	—
0·500	0·450	0·414	0·387	0·379	—	—
1·000	0·345	0·349	0·332	0·326	—	—

Accuracy of $f_{\pm}$ is better than $\pm 0·005$ for all values of concentration.

A. B. GARRETT et. al., J. Am. Chem. Soc., 1943, **65**, 1406.

TABLE

INDIVIDUAL ACTIVITY COEFFICIENTS OF IONS IN WATER AT

These values have been calculated from the equation: $\log f_i = \dfrac{-0.358\, z_i^2\, \Gamma''/s}{1 + 10^8\, a'_i\, 0.2325\, \Gamma''/s}$

hydrated ion and $\Gamma = 2I_{(m)}$.

Values of a'_i are derived by various methods (see KJELLAND, *loc. cit.*). The ions

Inorganic Ions	$10^8\, a'_i$	0·001
H'	9	0·975
Li'	6	·975
Rb', Cs', NH$_4$', Tl', Ag'	2·5	·975
K', Cl', Br', I', CN', NO$_2$', NO$_3$'	3	·975
OH', F', NCS', NCO', HS', ClO$_3$', ClO$_4$', BrO$_3$', IO$_4$', MnO$_4$'	3·5	·975
Na', CdCl', ClO$_2$', IO$_3$', HCO$_3$', H$_2$PO$_4$', HSO$_3$', H$_2$AsO$_4$', [Co(NH$_3$)$_4$(NO$_2$)$_2$]'	4·5	·975
Hg$_2$'', SO$_4$'', S$_2$O$_3$'', S$_2$O$_6$'', S$_2$O$_8$'', SeO$_4$'', CrO$_4$'', HPO$_4$''	4	·903
Pb'', CO$_3$'', SO$_3$'', MoO$_4$'', [Co(NH$_3$)$_5$Cl]'', [Fe(CN)$_5$NO]''	4·5	·903
Sr'', Ba'', Ra'', Cd'', Hg'', S'', S$_2$O$_4$'', WO$_4$''	5	·903
Ca'', Cu'', Zn'', Sn'', Mn'', Fe'', Ni'', Co''	6	·905
Mg'', Be''	8	·906
PO$_4$''', [Fe(CN)$_6$]''', [Cr(NH$_3$)$_6$]''', [Co(NH$_3$)$_6$]''', [Co(NH$_3$)$_5$H$_2$O]'''	4	·796
[Co(ethylenediamine)$_3$]'''	6	·796
Al''', Fe''', Cr''', Sc''', Y''', La''', In''', Ce''', Pr''', Nd''', Sm'''	9	·802
[Fe(CN)$_6$]''''	5	·668
[Co(S$_2$O$_3$)(CN)$_5$]''''	6	·670
Th'''', Zr'''', Ce'''', Sn''''	11	·678
[Co(SO$_3$)$_2$(CN)$_4$]'''''	9	·542
Organic Ions		
HCOO', citrate', CH$_3$NH$_3$', (CH$_3$)$_2$NH$_2$'	3·5	0·975
NH$_4$'.CH$_2$COOH, (CH$_3$).NH', C$_2$H$_5$NH$_3$'	4	·975
CH$_3$COO', CH$_2$ClCOO', (CH$_3$)$_4$N', (C$_2$H$_5$)$_2$NH$_2$', NH$_3$CH$_2$COO'	4·5	·975
CHCl$_2$COO', CCl$_3$COO', (C$_2$H$_5$)$_3$NH', (C$_3$H$_7$)NH$_3$'	5	·975
C$_6$H$_5$COO', C$_6$H$_4$OHCOO', C$_6$H$_4$ClCOO', C$_6$H$_5$CH$_2$COO', CH$_2$=CHCH$_2$COO', (CH$_3$)$_2$C=CHCOO', (C$_2$H$_5$)$_4$N', (C$_3$H$_7$)$_2$NH$_2$'	6	·975
(C$_6$H$_5$)(NO$_2$)$_2$O', (C$_3$H$_7$)$_2$NH', CH$_3$OC$_6$H$_4$COO'	7	·975
(C$_6$H$_5$)$_2$CHCOO', (C$_3$H$_7$)$_4$N'	8	·975
(COO)$_2$'', citrate''	4·5	·903
H$_2$C(COO)$_2$'', (CH$_2$COO)$_2$'', (CHOHCOO)$_2$''	5	·903
C$_6$H$_4$(COO)$_2$'', H$_2$C(CH$_2$COO)$_2$'', (CH$_2$CH$_2$COO)$_2$''	6	·905
OOC(CH$_2$)$_5$COO'', OOC(CH$_2$)$_6$COO'', Congo red anion''	7	·906
Citrate'''	5	·796

J. KIELLAND, *J. Am. Chem. Soc.*, 1937, 59, 1675.

III, 18

25 °C. CALCULATED FROM THE DEBYE-HÜCKEL THEORY

where f_i is the rational activity coefficient, a'_i is the effective diameter of the

are grouped according to their effective diameters of hydration, a'_i.

0·002	0·005	0·01	0·02	0·05	0·1	0·2
			total ionic concentration			
0·967	0·950	0·933	0·914	0·88	0·86	0·83
·965	·948	·929	·907	·87	·835	·80
·964	·945	·924	·898	·85	·80	·75
·964	·945	·925	·899	·85	·805	·755
·964	·946	·926	·900	·855	·81	·76
·964	·947	·928	·902	·86	·82	·775
·867	·803	·740	·660	·545	·445	·855
·868	·805	·742	·665	·55	·455	·87
·868	·805	·744	·67	·555	·405	·88
·870	·809	·749	·675	·57	·485	·405
·872	·813	·755	·69	·505	·52	·45
·725	·612	·505	·395	·25	·16	·095
·731	·620	·52	·415	·28	·195	·18
·738	·632	·54	·445	·325	·245	·18
·57	·425	·31	·20	·10	·048	·021
·575	·43	·315	·21	·105	·055	·027
·588	·455	·35	·255	·155	·10	·065
·43	·28	·18	·105	·045	·020	·009
·964	0·040	0·926	0·900	0·855	0·81	0·76
·964	·947	·927	·901	·855	·815	·77
·964	·947	·928	·902	·86	·82	·775
·964	·947	·928	·904	·865	·83	·79
·965	·948	·929	·907	·87	·835	·80
·965	·948	·930	·909	·875	·845	·81
·966	·949	·931	·912	·880	·85	·82
·867	·804	·741	·662	·55	·45	·36
·868	·805	·744	· 67	·555	·405	·88
·870	·809	·749	·675	·57	·485	·405
·872	·812	·755	·685	·58	·50	·425
·728	·616	·51	·405	·27	·18	115

TABLE III, 19

MEAN IONIC ACTIVITY COEFFICIENTS FOR SALTS IN ANHYDROUS AMMONIA AT 25 °C.

These activity coefficients $(f_\pm')$ are derived with reference to an arbitrary unit activity at molality of salt = 1.

NH₄NO₃		NH₄Cl		NH₄Br		NH₄I	
Molality	$f_\pm'$	Molality	$f_\pm'$	Molality	$f_\pm'$	Molality	$f_\pm'$
43·9	1·17	24·4	0·239	24·8	1·26	25·4	11·5
34·5	1·19	18·9	0·192	17·3	0·714	18·0	5·66
22·8	1·05	10·7	0·176	10·5	0·401	14·3	2·96
15·2	0·779	5·49	0·255	5·28	0·330	9·32	1·13
8·63	0·510	4·00	0·324	2·39	0·577	5·21	0·676
4·19	0·433	1·96	0·530	1·28	0·857	3·19	0·644
1·97	0·677	1·06	0·958	0·979	1·01	1·33	0·869
1·40	0·825	0·850	1·14	0·587	1·42	1·07	0·906
1·14	0·930	0·506	1·68	0·369	1·93	0·883	1·06
0·917	1·05			0·280	2·19	0·675	1·21
0·508	1·49					0·309	1·87
0·411	1·69						

W. E. LARSON and H. HUNT, *J. Phys. Chem.*, 1935, **39**, 877.

TABLE III, 20

ACTIVITY COEFFICIENTS OF HYDROGEN CHLORIDE IN ANHYDROUS ACETIC ACID AT 25 °C.

c (mols./l.)	$f_\pm$ (HCl)	c (mol/l.)	$f_\pm$ (HCl)
0·0004	2·81	0·0400	20·41
0·0016	4·87	0·0625	25·01
0·0036	7·06	0·0900	30·20
0·0064	9·08	0·1215	34·78
0·0100	13·80	0·1600	40·74
0·0225	15·80		

Accuracy: These values of $f_\pm$ are calculated from e.m.f. data accurate to $\pm 0·001$ v. The corresponding accuracy of $f_\pm$ is $\pm 0·005$.

B. O. HESTON and N. F. HALL, *J. Am. Chem. Soc.*, 1934, **56**, 1463.

TABLE III, 21

SALTING OUT CONSTANTS k', IN THE EQUATION $\log f_u = k' I_{(m)}$
(where $I_{(m)} =$ ionic strength, $f_u =$ activity of the non-electrolyte x).

Non-electrolyte/Salt	Ionic strength $I_{(m)}$	°C.	$k' = \dfrac{\log f_u}{I_{(m)}}$
H_2/HCl	0·505		0·0204
	1·019	25	0·0240
	2·080		0·0201
	3·186		0·0179
H_2/H_2SO_4	0·757		0·0169
	1·527	25	0·0193
	3·110		0·0183
$H_2/NaCl$	0·837		0·0942
	2·125	15	0·0970
	5·230		0·0889
H_2/KCl	0·534		0·0855
	1·086	15	0·0809
	3·171		0·0720
$H_2/MgSO_4$	1·732		0·0570
	6·520	15	0·0572
	10·00		0·0577
$H_2/CaCl_2$	0·963		0·0681
	3·366	15	0·0650
	8·870		0·0630
$H_2/AlCl_3$	3·200		0·0207
	6·250	15	0·0292
	11·28		0·0282
	19·74		0·0263
O_2/HCl	0·505		0·0386
	1·019	15	0·0367
	2·080		0·0322
O_2/H_2SO_4	0·758		0·0361
	1·527	15	0·0314
	3·108		0·0063

TABLE III, 21 (*Continued*)

Non-electrolyte/Salt	Ionic strength $I_{(m)}$	°C.	$k' = \dfrac{\log f_u}{I_{(m)}}$
$O_2/NaCl$	0·505		0·1328
	1·018	15	0·1299
	2·072		0·1320
O_2/K_2SO_4	0·760	15	0·1081
	1·563		0·1070
$N_2/NaCl$	0·115		0·346
	0·372	25	0·209
	1·170		0·197
	2·270		0·205
$N_2/BaCl_2$	0·509		0·153
	1·070	25	0·123
	2·310		0·108
N_2O/HCl	0·505	15	0·0188
	1·018		0·0151
N_2O/H_2SO_4	0·757		0·0280
	1·527	15	0·0253
	3·108		0·0213
$N_2O/LiCl$	0·505	15	0·0877
	1·019		0·0869
$N_2O/NaCl$	1·178		0·1059
	2·426	15	0·1034
	4·761		0·0940
N_2O/KCl	0·508	15	0·0954
	1·031		0·0858
$N_2O/RbCl$	0·509	15	0·0806
	1·036		0·0767
$N_2O/CsCl$	0·511	15	0·0591

TABLE III, 21 (*Continued*)

Non-electrolyte/Salt	Ionic strength $I_{(m)}$	°C.	$k' = \dfrac{\log f_n}{I_{(m)}}$
$N_2O/CaCl_2$	2·801	15	0·0652
	0·810		0·0031
$N_2O/Al(NO_3)_3$	2·972	15	0·0520
	6·144		0·0375
Benzoic acid/NaCl	0·01982		0·153
	0·05010		0·197
	0·1002	25	0·191
	0·2009		0·190
	0·5022		0·180
Benzoic acid/KCl	0·02004		0·130
	0·05008		0·172
	0·1001	25	0·162
	0·2008		0·152
	0·5074		0·130
Benzoic acid/BaCl₂	0·03441		0·101
	0·1425		0·099
	0·2098	25	0·097
	0·6048		0·100
o-Toluic acid/NaCl	0·01200		0·217
	0·05000		0·231
	0·1000	25	0·237
	0·2500		0·220
o-Toluic acid/BaCl₂	0·03600		0·203
	0·1494		0·134
	0·3000	25	0·133
	0·7500		0·123
o-Nitrobenzoic acid/NaCl	0·02005		0·194
	0·05003		0·180
	0·1002	25	0·187
	0·4967		0·192
	0·0983		0·184

TABLE III, 21 (*Continued*)

Non-electrolyte/salt	Ionic strength $I_{(m)}$	°C.	$k' = \dfrac{\log f_s}{I_{(m)}}$
o-Nitrobenzoic acid/BaCl$_2$	0·03726		—0·086
	0·1499		0·103
	0·2963	25	0·096
	0·7383		0·118
Acetic acid/LiCl	0·100		0·073
	0·251	25	0·078
	0·505		0·039
	1·560		0·079
Acetic acid/NaCl	0·1001		0·056
	0·251		0·065
	0·5045	25	0·062
	1·018		0·064
	2·072		0·063
Acetic acid/KCl	0·1003		0·026
	0·2520		0·026
	0·5075	25	0·027
	1·031		0·026
Acetic acid/MgSO$_4$	0·4		0·014
	1·0		0·018
	2·0	25	0·020
	4·0		0·022
	8·0		0·025
Phenylthiourea/LiNO$_3$	0·125		—0·0186
	0·252		—0·0154
	0·507	20	—0·0120
	1·031		—0·0067
Phenylthiourea/NaCl	0·125		0·1632
	0·251		0·1362
	0·505	20	0·1283
	1·018		0·1333

TABLE III, 21 (*Continued*)

Non-electrolyte/Salt	Ionic strength $I_{(m)}$	°C.	$k' = \dfrac{\log f_u}{I_{(m)}}$
Phenylthiourea/KCl	0·125		0·1232
	0·252	20	0·1436
	0·508		0·1021
	1·081		0·1046
Phenylthiourea/BaCl₂	0·189		0·1381
	0·376	20	0·0845
	1·528		0·0780
	3·093		0·0652
Phenylthiourea/AlCl₃	0·250		0·1272
	0·500	20	0·0724
	1·003		0·0024
	2·014		0·0559

M. RANDALL and C. F. FAILEY, *Chem. Rev.*, 1927, **4**, 271.

TABLE III, 22

SALTING OUT RATIO CONSTANTS *

* *The salting out ratio constant* is defined by the equation $\dfrac{\Delta s}{s_0} = kc$ and approximates to the salting out constant $\log \dfrac{s_0}{s}$,

where s_0 is the solubility of the non-electrolyte in the pure solvent and s is the solubility of the non-electrolyte in a solution of electrolyte in the same solvent under the same conditions.

$\Delta s = (s_0 - s) =$ the salting out of the non-electrolyte.

Solvent composition is given as wt.%.

See J. O'M. BOCKRIS and H. EGAN, *Trans. Faraday Soc.*, unpublished.

(Electrolyte concentration expressed as molality)				
Non-electrolyte/Salt	Solvent	°C.	Concentration of electrolyte	k (= salting out ratio constant)
N₂/NaCl	H₂O	25	1·000	0·19
		35	1·000	0·26
		45	1·000	0·45
		55	1·000	0·49
		65	1·000	0·48

TABLE III, 22 (*Continued*)

Non-electrolyte/Salt	Solvent	°C.	Concentration of electrolyte	k (= salting out ratio constant)
N₂/NaCl	EtOH/H₂O			
	0·0% EtOH	25	1·025	
	10·0% EtOH	25	1·025	0·02
	14·0% EtOH	25	1·025	0·04
	22·0% EtOH	25	1·025	0·07
	27·1% EtOH	25	1·025	0·12
	84·9% EtOH	25	1·025	0·15
	44·7% EtOH	25	1·025	0·18
	Dioxan/H₂O			
	0·0% Dioxan	25	1·025	
	5·8% Dioxan	25	1·025	—0·88
	11·0% Dioxan	25	1·025	—1·18
	20·7% Dioxan	25	1·025	—0·66
	24·1% Dioxan	25	1·025	—0·54
	80·7% Dioxan	25	1·025	—0·27
Benzoic acid/NaF	EtOH/H₂O			
	0·0% EtOH	25	0·500	—2·06
	11·0% EtOH	25	0·500	—1·56
	18·8% EtOH	25	0·500	—1·27
	24·8% EtOH	25	0·500	—1·08
Benzoic acid/NaCl	H₂O	30	1·000	0·82
		35	1·000	0·82
		45	1·000	0·88
		55	1·000	0·84
		65	1·000	0·86
		75	1·000	0·86
	MeOH/H₂O			
	0·0% MeOH	25	1·025	0·82
	5·8% MeOH	25	1·025	0·80
	10·1% MeOH	25	1·025	0·27
	20·5% MeOH	25	1·025	0·21
	80·4% MeOH	25	1·025	0·15
	40·7% MeOH	25	1·025	0·11
	52·6% MeOH	25	1·025	0·09
	62·0% MeOH	25	1·025	0·09

TABLE III, 22 (*Continued*)

Non-electrolyte/Salt	Solvent	°C.	Concentration of electrolyte	k (= salting out ratio constant)
Benzoic acid/NaCl	5·5% EtOH	25	1·025	0·27
	10·0% EtOH	25	1·025	0·24
	20·1% EtOH	25	1·025	0·04
	30·6% EtOH	25	1·025	—0·11
	40·2% EtOH	25	1·025	—0·06
	49·7% EtOH	25	1·025	0·01
	54·6% EtOH	25	1·025	0·01
	13·6% EtOH	25	0·100	0·27
	20·4% EtOH	25	0·100	0·11
	31·4% EtOH	25	0·100	0·02
	42·0% EtOH	25	0·100	—0·05
	49·8% EtOH	25	0·100	—0·005
	58·1% EtOH	25	0·100	0·18
	67·8% EtOH	25	0·100	0·36
	76·0% EtOH	25	0·100	0·58
	H_2O	25	0·100	0·43
	5·1% Dioxan	25	1·025	0·30
	10·0% Dioxan	25	1·025	0·29
	20·0% Dioxan	25	1·025	0·22
	24·2% Dioxan	25	1·025	0·17
Benzoic acid/NaCl	H_2O	25	2·000	0·269
		25	3·500	0·201
		25	5·000	0·153
		25	6·000	0·137
Benzoic acid/NEt₄I	H_2O	25	0·500	—1·75
	11·0% EtOH	25	0;500	—2·51
	18·8% EtOH	25	0·500	—1·74
	24·8% EtOH	25	0·500	—1·63
	37·6% EtOH	25	0·500	—0·55

TABLE III, 22 (*Continued*)

Non-electrolyte/Salt	Solvent	°C.	Concentration of electrolyte	k (= salting out ratio constant)
Hydroquinone/HI	H_2O	25	0·250	0·17
Hydroquinone/NMe$_4$I	H_2O	25	0·100	—1·15
		25	0·250	—0·69
Hydroquinone/NPr$_4$I	H_2O	25	0·100	—4·7
		25	0·250	—2·3
Hydroquinone/NEt$_4$I	H_2O	25	0·100	—3·1)
		25	0·250	—1·23
Hydroquinone/NH$_4$I	H_2O	25	0·100	0·10
		25	0·250	0·03
Mannitol/NaCl	H_2O	25	1·025	0·12
		35	1·025	0·05
		45	1·025	0·04
		55	1·025	0·04
		25	0·513	0·14
		25	1·537	0·11
	10·5% MeOH	25	1·025	—0·08
	20·7% MeOH	25	1·025	—0·36
	32·2% MeOH	25	1·025	—0·65
	17·6% EtOH	25	1·025	—0·07
	21·7% EtOH	25	1·025	—0·18
	30·7% EtOH	25	1·025	—0·31
	42·4% EtOH	25	1·025	—0·51

TABLE III, 22 (*Continued*)

Non electrolyte/Salt	Solvent	°C.	Concentration of electrolyte	k (= salting out ratio constant)
Mannitol/BaCl$_2$	H$_2$O	25	1·025	0·249
		35	1·025	—0·126
		45	1·025	—0·187
		55	1·025	—0·213
		25	0·513	0·410
		25	1·537	0·234
	10·5% MeOH	25	1·025	—0·190
	10·5% MeOH	25	1·025	—0·435
Mannitol/MgCl$_2$	H$_2$O	25	1·025	0·133
		35	1·025	0·087
		45	1·025	0·117
		55	1·025	0·246
		25	0·513	0·243
		25	1·537	0·097
	10·5% McOH	25	1·025	—0·005
	20·7% MeOH	25	1·025	—0·250
	32·2% MeOH	25	1·025	—0·054
Mannitol/AlCl$_3$	H$_2$O	25	1·025	0·180
		35	1·025	—0·126
		45	1·025	—0·005
		55	1·025	0·144
		25	0·513	0·176
		25	1·537	0·211

TABLE III, 22 (*Continued*)

Non-electrolyte/Salt	Solvent	°C.	Concentration of electrolyte	k (= salting out ratio constant)
Mannitol/AlCl₃ (*Contd.*)	10·5% MeOH	25	1·025	—0·085
	20·7% MeOH	25	1·025	—0·129
	82·2% MeOH	25	1·025	—0·087
Cinchonine/NaI	McOH	25	0·500	0·280
		25	1·000	0·229
		25	2·000	0·152
		25	2·500	0·128
		25	8·000	0·110
		25	8·500	0·104
	EtOH	25	0·500	0·240
		25	1·000	0·242
		25	1·500	0·206
	n-PrOH	25	1·000	0·265
	n-BuOH	25	1·000	0·302
	n-AmOH	25	1·000	0·402
	i-PrOH	25	1·000	0·254
	sec-BuOH	25	1·000	—0·369
	acetone	25	1·000	—0·609
	Methyl ethyl ketone	25	1·000	—2·818
Phenylthiourea/NaCl	H₂O	25	1·000	0·81
		35	1·000	0·80
		45	1·000	0·29
		55	1·000	0·81
		65	1·000	0·84
		75	1·000	0·86

J. O'M. Bockris and H. Egan, *Trans. Faraday Soc.*, unpublished.

TABLE III, 28

ACTIVITY COEFFICIENTS OF FUSED SALTS

AgCl in PbCl$_2$							
Mol. Fraction AgCl	1·00	0·8	0·6	0·45	0·8	0·2	0·1
$f_{\pm}$ (500 °C.)	1·000	1·001	0·980	0·982	0·980	0·981	1·021
$f_{\pm}$ (600 °C.)	1·000	1·000	0·980	0·980	0·982	0·993	1·034

E. J. SALSTRÖM, *J. Am. Chem. Soc.*, 1034, 56, 1272.

PbBr$_2$ in PbCl$_2$					
Mol. Fraction PbBr$_2$	1·00	0·80	0·00	0·50	0·45
$f_{\pm}$ (450° C.)	1·000	0·873	0·766	0·682	0·588
$f_{\pm}$ (500 °C.)	1·000	0·586	0·737	0·667	0·581
$f_{\pm}$ (550 °C.)	1·000	0·845	0·713	0·652	0·576

E. J. SALSTRÖM and J. H. HILDEBRAND, *J. Am. Chem. Soc.*, 1930, 52, 4041.

AgBr in LiBr					
Mol. Fraction AgBr	1·0000	0·5937	0·4086	0·2548	0·1100
$f_{\pm}$ (500 °C.)	1·0000	1·211	1·477	2·040	2·651
$f_{\pm}$ (550 °C.)	1·0000	1·199	1·432	1·050	2·457
$f_{\pm}$ (600 °C.)	1·0000	1·194	1·408	1·887	2·303

E. J. SALSTRÖM and J. H. HILDEBRAND, *J. Am. Chem. Soc.*, 1930, 52, 4050.

TABLE III, 23 (*Continued*)

PbCl₂ in ZnCl₂						
Mol. Fraction PbCl₂	1·000	0·885	0·688	0·595	0·490	0·801
$f_\pm$ 500 °C.	1·000	0·080	0·865	0·770	0·675	0·575
$f_\pm$ 600 °C.	1·000	0·945	0·840	0·750	0·685	0·515

Accuracy of these determinations: e.m.f. measured to $\pm 0\cdot 2$ mv. Calculated $f_\pm$ accurate to $\pm 0\cdot 001$.

A. WACHTER and J. H. HILDEBRAND, *J. Am. Chem. Soc.*, 1980, **52**, 4655.

TABLE III, 24

HYDRATION NUMBERS OF UNIVALENT IONS IN AQUEOUS SOLUTION AT 25 °C.

Ion	Activity ([1])	Density ([2])	Compressibility ([3]) **	Entropy ([4])	Mobility ([5])	Calcd. ([6])
Li˙	6	6	8	5	5	6
Na˙	—	4	4	4	4	4·5
K˙	0	4	8	2	4 *	2·9
Rb˙	—	0	—	2	—	2·3
Cs˙	—	0	—	—	—	0
F′	—	4	5	5	—	4·7
Cl′	2·6	0	8	2	4 *	2·9
Br′	—	0	—	1·5	—	2·4
I′	—	0	2	0·5	0·7 *	0

[1] N. BJERRUM, *Z. asiorg, Chem.*, 1920, **109**, 275.

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[5] H. ULICH, *Trans. Faraday Soc.*, 1927, **23**, 802.

[6] J. O'M. BOCKRIS, *Quarterley Reviews*, 1949, **III**, 173.

* Extrapolated from some results in alcoholic solutions. STOKES' law is not applicable for these ions in aqueous solutions.

** Calculated for individual ions on the approximate assumption that K˙ and Cl′ are equally hydrated in aq. solutions of KCl.

TABLE III, 25

HEATS OF HYDRATION OF IONS IN k.cal./g.ion

Ion	BERNAL & FOWLER (¹)		WEBB (²)	LATIMER (³)	VERWEY (⁴)
	calc.	obs. *			
H˙	276				
Li˙	186	181		114·6	112·5
Na˙	114	116	99	89·7	88·5
K˙	94	92	81·9	78·5	72
Rb˙	87	87	76·9	67·5	66·5
Cs˙	80	79	71·5	60·8	59
Tl˙	140	107	78·6		
Ag˙	174	102	95·5		108
NH₄˙	87	87			
Be˙˙	608	600			
Mg˙˙	490	495			
Ca˙˙	410	410			
Sr˙˙	370	370			
Ba˙˙	346	350			
Zn˙˙	626	528	525		
Fe˙˙	501	500			
Cd˙˙	596	462	473		
Co˙˙	580	500			
Ni˙˙	594	516			
Cu˙˙	645	536			
Mn˙˙	534	479			
Hg˙˙	672	480	486		
Al˙˙˙	1149	1149			
F′	97	94	87	118·9	114
Cl′	65	67	70·1	84·2	86
Br′	57	63	66·2	78	80·5
I′	47	49	61·5	70	72·5

[1] *J. Chem. Phys.*, 1933, 1, 515.
[2] *J. Am. Chem. Soc.*, 1926, 48, 2589.
[3] *J. Chem. Phys.*, 1939, 7, 108.
[4] *Rec. Trav. Chim.*, 1941, 60, 887.
See also vol. I, Table 10, p. 124.

* Calculated from experimental values for KF according to procedure described on pp. 122—123.

TABLE III, 26

VALUES OF THE CONSTANTS APPEARING IN THE LIMITING SLOPE OF THE ONSAGER EQUATION: $\Lambda_y = \Lambda_\infty - (A + B\Lambda_\infty)\sqrt{c}$, FOR CONDUCTANCE IN 1:1 AQUEOUS ELECTROLYTE SOLUTIONS

Temp. °C.	B	A
0	0·2198	29·47
5	·2205	34·87
10	·2220	40·56
15	·2237	46·35
18	·2240	50·31
20	·2257	52·95
25	·2277	59·86
30	·2299	67·15
35	·2322	74·81
40	·2348	82·79
45	·2374	90·99
50	·2401	99·28
55	·2431	107·98
60	·2461	116·98

Accuracy: In calculation of B, viscosities are accurate to $\pm 0.1\%$ from 0 to 40 °C. For higher temperatures viscosities are accurate to $\pm 0.5 - 1\%$.
The values of B are of the same accuracy. See International Critical Tables V, 10.
From H. S. HARNED and B. B. OWEN, *Physical Chemistry of Electrolytic Solutions*, Reinhold, New York, 1943, p. 128.

TABLE III, 27

EQUIVALENT CONDUCTANCES OF SALTS AT 25 °C. FOR VARIOUS DILUTIONS

(c in g.equiv./l.)

c \ Salt	0	0·0005	0·001	0·005	0·01	0·02	0·05	0·1	Ref.
HCl	426·16	422·74	421·36	415·80	412·00	407·24	399·09	391·32	1, 19
LiCl	115·03	113·15	112·40	109·40	107·32	104·65	100·11	95·86	1, 2, 8
NaCl	126·45	124·50	123·74	120·65	118·51	115·76	111·06	106·74	4, 20
KCl	149·86	147·81	146·95	143·55	141·27	138·34	133·37	128·96	1, 20

TABLE III, 27 (Continued)

Salt \ c	0	0·0005	0·001	0·005	0·01	0·02	0·05	0·1	Ref.
NH_4Cl	149·7	—	—	—	141·28	138·33	133·29	128·75	5
KBr	151·9	—	—	146·09	143·43	140·48	135·08	131·39	6, 7
NaI	126·94	125·36	124·25	121·25	119·24	116·70	112·79	108·78	8
KI	150·38	—	—	144·37	142·18	139·45	134·97	131·11	7
KNO_3	144·96	142·77	141·84	138·48	132·82	132·41	126·31	120·40	1
$KHCO_3$	118·00	116·10	115·34	112·24	110·08	107·22	—	—	9
NaO_2CCH_3	91·0	89·2	88·5	85·72	83·76	81·24	76·92	72·80	10
$NaO_2C(CH_3)_2$ – CH_3	82·70	81·04	80·31	77·58	75·76	73·39	69·32	65·27	11
NaOH	247·8	245·6	244·7	240·8	238·0	—	—	—	18
$AgNO_3$	133·36	131·36	130·51	127·20	124·76	121·41	115·24	109·14	1
$MgCl_2$	129·40	125·61	124·11	118·31	114·55	110·04	103·08	97·10	12
$CaCl_2$	135·84	131·93	130·36	124·25	120·36	115·65	108·47	102·46	12
$SrCl_2$	135·80	131·90	130·33	124·24	120·29	115·54	108·25	102·19	12
$BaCl_2$	139·98	135·90	134·34	128·02	123·94	119·09	111·48	105·19	12
Na_2SO_4	129·9	125·74	124·15	117·15	112·44	106·78	97·75	89·08	7
$CuSO_4$	133·6	121·6	115·26	94·07	83·12	72·20	59·05	50·58	13
$ZnSO_4$	132·8	121·4	114·53	95·49	84·91	74·24	61·20	52·64	13
$LaCl_3$	145·8	139·6	137·0	127·5	121·8	115·3	106·2	99·1	6, 14
$K_3Fe(CN)_6$	174·5	166·4	163·1	150·7	—	—	—	—	15
$K_4Fe(CN)_6$	184·5	—	167·24	146·09	134·83	122·82	107·70	97·87	16, 17
KIO_4	127·92	125·80	124·94	121·24	118·51	114·14	106·72	98·12	23
$KReO_4$	128·20	126·03	125·12	121·31	118·49	114·49	106·40	97·40	23
$LiClO_4$	105·08	104·18	103·44	100·57	98·61	96·18	92·20	88·56	22
$NaClO_4$	117·48	115·64	114·87	111·75	109·59	106·96	102·40	98·43	22
$KClO_4$	140·04	138·76	137·87	134·16	131·46	127·92	121·02	115·20	22

Accuracy: $\pm$ 0·02%

EQUIVALENT CONDUCTANCES OF BROMATES AND PERCHLORATES AT 25 °C. FOR VARIOUS DILUTIONS

(c in g.mol/l. Λ_v = equivalent conductance)

$KBrO_3$		$NaBrO_3$		$AgClO_4$	
c	Λ_v	c	Λ_v	c	Λ_v
0·14774	103·02	0·48193	75·07	0·0010256	123·43
0·093616	107·53	0·10579	85·93	0·0020782	121·14
0·049083	112·26	0·057283	89·97	0·006093	118·57
0·011069	120·37	0·010836	97·97	0·011165	116·88

TABLE III, 27 (*Continued*)

KBrO₃		NaBrO₃		AgClO₄	
c	*Λᵧ*	*c*	*Λᵧ*	*c*	*Λᵧ*
0·0082819	124·88	0·0053688	100·12	0·061064	104·82
0·0010518	126·48	0·0010531	103·28	0·13680	96·50
0·0005443	127·27	0·0005078	104·12	0·28488	87·75
0	129·81	0	105·86	0	126·57
Accuracy: ±0·05%		Accuracy: ±0·05%.		Accuracy: ±0·1%.	
Reference 21.		*Reference* 21.		*Reference* 24.	

For the temperature dependence of conductance of some of the salts in the above tables see references 19 and 20.

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[23] J. H. JONES, *ibid.*, 1946, 68, 240.

[24] J. H. JONES, *ibid.*, 1947, 69, 2065.

See also vol. I, Table 14, p. 146.

TABLE III, 28

TEMPERATURE DEPENDENCE OF THE CONDUCTANCE OF KCl, KBr AND NaCl IN
AQUEOUS SOLUTION

KBr.	$10^4 c. = 0$ *	5	10	20	50	100	Ref.
15 °C.	122·8	121·22	120·57	119·69	128·02	116·3	(1)
25 °C.	151·64	149·60	141·73	147·64	145·49	143·23	(1)
35 °C.	182·24	179·76	178·74	177·34	174·70	171·94	(1)
45 °C.	214·17	211·07	209·84	208·18	204·91	201·53	(1)
							* (2)

c in g.mol/l.

TEMPERATURE DEPENDENCE OF IONIC MOBILITIES l_∞ AT INFINITE DILUTION
(*cf.* Table III, 30)

Ion	15 °C.	25 °C.	35 °C.	40 °C.	Ref.
Cl′ (KCl)	61·41	76·35	92·21	108·92	(2)
Cl′ (NaCl)	61·43	76·35	92·22	108·88	,,
Br′ (KBr)	63·15	78·14	94·08	110·08	,,
K· (KCl)	59·66	73·50	88·21	103·49	,,
Na· (NaCl)	39·75	50·10	61·53	73·77	,,
H· (HCl)	300·6	349·82	397·0	441·4	,,
Li· (LiCl)	(18 °C.)				
	33·03	38·68			

And $\Lambda_{(LiCl)} = 60·559 \ (1 + 0·00314 \ t + 0·0001137 \ t^2)$ where t is in °C.   (3)

TEMPERATURE DEPENDENCE OF CONDUCTANCE OF KCl, KBr AND NaCl

Values of $\dfrac{d(\ln l_\infty)}{dT}$.

Ion	15 °C.	25 °C.	35 °C.	45 °C.
Cl′	0·02340	0·02020	0·01765	0·01570
Br′	0·02285	0·01930	0·01730	0·01585
K·	0·02235	0·01950	0·01705	0·01500
Na·	0·02445	0·02160	0·01930	0·01695
	0·01655	0·01385	0·01155	0·00970

[1] H. E. GUNNING and A. R. GORDON, *J. Chem. Phys.*, 1943, 11, 18.
[2] G. C. BENSON and A. R. GORDON, *J. Chem. Phys.*, 1945, 13, 473.
(See also *J. Chem. Phys.*, 1942, 10, 120).
[3] M. M. JACOPETTI, *Gazz. Chim. Ital.*, 1942, 72, 251.
(See also F. GIORDANO and T. MARESCA, *ibid.*, 1929, 59, 878, 892).

TABLE III, 29

ABSOLUTE ION VELOCITIES IN cm.^{2} sec.$^{-1}$ volt^{-1}. 10^5 AT 18 °C. IN AQUEOUS SOLUTIONS

Ion	Compound studied	Concentration in g.equivalent/cc.						
		10^{-7}	2.10^{-7}	5.10^{-7}	10^{-6}	2.10^{-6}	5.10^{-6}	10^{-5}
Ca··	Ca(OH)₂	—	48·0	46·5	46·2	40·5	—	—
Ba··	Ba(OH)₂	—	—	—	47·8	43·5	—	—
Na·	NaOAc *	—	47·8	—	—	44·2	—	41·5
K·	KOAc	—	—	67·0	65·5	—	—	—
Li·	LiOAc	—	—	—	—	30·0	—	—
NH₄·	NH₄OAc	—	68·0	—	—	—	60·5	57·5
Ca··	Ca(OAc)₂	—	53·0	—	52·5	50·0	—	—
Cu··	Cu(OAc)₂	—	—	—	42·5	40·7	—	38·0
Ni··	Ni(OAc)₂	—	—	47·2	—	47·0	—	—
Mn··	Mn(OAc)₂	—	—	—	46·5	48·3	—	—
Pb··	Pb(OAc)₂	—	—	56·5	51·5	48·5	—	—
Zn··	Zn(OAc)₂	—	—	46·5	47·2	45·5	41·0	—
Al···	Al(OAc)₃	—	—	—	46·0	42·5	—	—
NH₄·	(NH₄)₂S₂O₈	—	—	71·0	71·0	60·5	—	—
NH₄·	(NH₄)₂CrO₄	—	—	63·0	64·1	64·0	—	—
NH₄·	(NH₄)₂CO₃	—	—	—	—	32·5	35·5	—
Cl′	HCl	68·0	67·5	66·5	—	—	—	—
SO₄″	H₂SO₄	73·0	71·5	69·5	60·5	—	—	—
NO₃′	HNO₃	—	—	—	—	—	58·5	57·5
PO₄‴	H₃PO₄	47·0	36·0	28·5	28·5	27·5	—	—
Picrate	Picric acid	—	27·0	—	28·0	—	—	.....
Oxalate	Oxalic acid	—	39·0	38·5	36·7	—	—	—
Maleate	Maleic acid	—	—	—	37·5	35·0	—	—
Fumarate	Fumaric acid	—	—	—	—	20·5	—	—
Salicylate	Salicylic acid	—	—	24·0	21·0	19·0	—	—
Tartrate	Tartaric acid	—	—	24·0	21·0	18·0	16·1	—
Formate	Formic acid	—	—	—	21·0	14·5	—	—
Chloracetate	Chloracetic acid	—	—	30·5	26·5	25·0	—	—
Trichlor-acetate	Trichloracetic acid	33·0	30·5	30·0	—	—	—	—

Reproducibility not better than ±2%.   * OAc = acetate.

J. CLERIN, *Ann. Chim.*, 1945, 20, 244.

TABLE III, 80

LIMITING IONIC CONDUCTANCES (l_∞) IN WATER AT 25 °C.

Cation	l_∞	Ref.	Anion	l_∞	Ref.
H·	349·8	1, 18, 19	OH′	197·6	8, 22
Li·	38·69	1, 27	Cl′	76.84	1, 19, 21
Na·	50·11	1, 18, 21	Br′	78·3	9, 2
K·	73·52	1, 21	I′	76·8	10, 2
NH₄·	73·4	2	NO₃′	71·44	1
Ag·	61·92	1	HCO₃′	44·5	11
Tl·	74·7	3	HCO₂′	54·6	18
¹/₂Mg··	53·06	4	CH₃CO₂′	40·9	1, 13
¹/₂Ca··	59·50	4	ClCH₂CO₂′	39·8	12, 13
¹/₂Sr··	59·46	4	CH₂CH₂CO₂′	35·8	14
¹/₂Ba··	63·64	4	CNCH₂CO₂′	41·8	18
¹/₂Cu··	54	5	CH₃(CH₂)₂CO₂′	32·6	14, 18
¹/₂Zn··	53	5	C₆H₅CO₂′	32·3	15, 16
¹/₃La···	69·5	6, 2	HC₂O₄′	40·2	20
¹/₃Co(NH₃)₆····	102·3	7	¹/₂C₂O₄″	24·0	20
			¹/₂SO₄″	80	2, 7
			¹/₃Fe(CN)₆‴	101	7
			¹/₄Fe(CN)₆⁗	111	17
			IO₄′	54·38	28
			ReO₄′	54·68	28
			ClO₄′	67·32 ± 0·06	24 (cf. 26)
			BrO₃′	55·78 ± 0·05	25

References:

All values have been corrected to conform to the standard of G. JONES and B. C. BRADSHAW ²⁸.

¹ D. A. McINNES, T. SHEDLOVSKY and L. G. LONGSWORTH, *J. Am. Chem. Soc.*, 1932, 54, 2758.

² D. A. McINNES, *J. Franklin Inst.*, 1938, 225, 661.

³ R. A. ROBINSON and C. W. DAVIES, *J. Chem. Soc.*, 1937, 139, 574.

⁴ T. SHEDLOVSKY and A. S. BROWN, *J. Am. Chem. Soc.*, 1934, 56, 1066.

⁵ B. B. OWEN and B. W. GURRY, *ibid.*, 1938, 60, 3074.

⁶ G. JONES and C. F. BICKFORD, *ibid.*, 1934, 56, 602.

⁷ G. S. HARTLEY and G. W. DONALDSON, *Trans. Faraday Soc.*, 1937, 33, 457.

⁸ V. SIVERTZ, R. E. REITMEIER and H. V. TARTAR, *J. Am. Chem. Soc.*, 1940, 62, 1379.

⁹ G. JONES and C. F. BICKFORD, *ibid.*, 1934, 56, 602.

¹⁰ P. A. LASSELLE and J. G. ASTON, *ibid.*, 1933, 55, 3067.

¹¹ T. SHEDLOVSKY and D. A. MacINNES, *ibid.*, 1935, 57, 1705.

TABLE III, 30 (*Continued*)

[12] T. SHEDLOVSKY, A. S. BROWN and D. A. McINNES, *Trans. Electrochem. Soc.*, 1935, **66**, 165.

[13] B. SAXTON and T. W. LANGER, *J. Am. Chem. Soc.*, 1933, **55**, 3638.

[14] D. BELCHER, *ibid.*, 1938, **60**, 2744.

[15] B. SAXTON and H. F. MEIER, *ibid.*, 1934, **56**, 1918. These authors also report 30·3 and 31·0 for the ortho and meta chlorobenzoate ions respectively.

[16] F. G. BROCKMAN and M. KILPATRICK, *ibid.*, 1934, **56**, 1483.

[17] G. JONES and F. C. JELEN, *ibid.*, 1936, **58**, 2581; C. W. DAVIES, *ibid.*, 1937, **59**, 1760.

[18] B. SAXTON and L. S. DARKEN, *J. Am. Chem. Soc.*, 1940, **62**, 846.

[19] Values at 10° intervals are given by B. B. OWEN and F. H. SWEETON, *ibid.*, 1941, **63**, 2811.

[20] L. S. DARKEN, *ibid.*, 1941, **63**, 1007.

[21] Values at 15, 25, 35 and 45° are given by H. E. GUNNING and A. R. GORDON, *J. Chem. Phys.*, 1942, **10**, 126.
See also N. C. LI and W. BRULL, *J. Am. Chem. Soc.*, 1942, **64**, 1685 and A. R. GORDON, *ibid.*, 1942, **64**, 2517.

[22] L. S. DARKEN and H. F. MEIER, *ibid.*, 1942, **64**, 621.

[23] J. H. JONES, *ibid.*, 1946, **68**, 240.

[24] J. H. JONES, *ibid.*, 1945, **67**, 855.

[25] J. H. JONES, *ibid.*, 1944, **66**, 1115.

[26] J. H. JONES, *ibid.*, 1947, **69**, 2065.

[27] M. M. JACOPETTI, *Gazz. Chim. Ital.*, 1942, **72**, 251.

[28] G. H. JONES and BRADSHAW, *J. Am. Chem. Soc.*, 1933, **55**, 1780.

See also Tables III, 28 and 29; and the exemplifying summary in Chapter VI, Table 10.

TABLE III, 31

DIELECTRIC CONSTANTS (ε) OF AQUEOUS ELECTROLYTE SOLUTIONS AT 25 °C. FOR WAVE LENGTHS OF 3 AND 10 cm.

ε_s = static dielectric constant of the solution.

Salt	Normality	$\varepsilon_{3\ cm.}$	$\varepsilon_{10\ cm.}$	ε_s
LiCl	0·5	26·0	10·7	71·2
	1·0	23·3	8·0	64·2
	1·5	20·2	5·0	57·0
	2·0	17·0	—	51·0

TABLE III, 31 (*Continued*)

Salt	Normality	$\varepsilon_{1\ cm.}$	$\varepsilon_{10\ cm.}$	ε_s
RbCl	0·5	25·0	8·9	73·5
	1·0	23·2	9·4	68·5
	1·5	22·0	—	63·5
	2·0	20·2	—	58·5
KCl	0·5	25·9	10·5	73·5
	1·0	23·6	6·8	68·5
	1·5	21·8	—	63·5
	2·0	18·4	—	58·5
BaCl$_2$	1·0	22·2	8·8	64·0
	2·0	16·9	—	51·0
HCl	0·25	26·0	7·8	72·5
	0·5	26·3	—	69·0
NaOH	0·25	26·6	11·7	73·0
	0 5	24·7	4·9	68·0
KI	0·198	27·2	10·4	75·0
	0·396	25·1	11·1	72·0
NaF	0·415	25·0	7·4	73·0
	0·830	24·0	8·4	69·0
LaCl$_3$	0·52	25·2	8·9	71·0
	1·04	22·0	7·8	64·0
KF	0·242	27·0	8·8	75·0
	0·484	25·7	7·3	72·0
NaI	0·428	25·1	8·3	71·0
	0·856	20·8	—	64·0
MgCl$_2$	0·408	25·2	18·0	71·0
	0·935	23·0	8·1	64·5
Na$_2$SO$_4$	0·5	26·4	—	73·0
	1·0	25·1	—	67·0
	2·0	20·8	—	60·5

Accuracies: $\varepsilon_{1\ cm.}$, $\pm 1\cdot 0$, $\varepsilon_{10\ cm.}$, ± 3, ε_s, ± 2.
For frequency dependence of ε see original paper.

J. B. HASTED, D. M. RITSON and C. H. COLLIE, *J. Chem. Phys.*, 1948, 16, 1.

TABLE III, 32

DIFFERENTIAL DIFFUSION COEFFICIENTS AT 25 °C. FOR AQUEOUS SOLUTIONS

D in cm.^{2}/sec. . 10^5; c in mol/l.

For $c = 0$ the values are the NERNST limiting values.

c	Electrolyte							
	$D . 10^5$ cm.^{2}/sec.							
	HCl	HBr	LiCl	LiBr	NaCl	NaBr	KCl	KBr
0	3·34	3·403	1·368	1·379	1·612	1·627	1·995	2·078
0·05	3·07	3·156	1·280	1·300	1·506	1·533	1·863	1·892
0·1	3·05	3·146	1·269	1·289	1·484	1·517	1·848	1·874
0·2	3·06	3·190	1·267	1·285	1·478	1·507	1·835	1·870
0·3	3·09	3·249	1·269	1·296	1·477	1·515	1·826	1·872
0·5	3·18	3·388	1·278	1·328	1·474	1·542	1·835	1·880
0·7	3·28	3·552	1·288	1·360	1·475	1·569	1·846	1·917
1·0	3·43	3·869	1·302	1·404	1·483	1·596	1·876	1·975
1·5	3·74	—	1·331	1·473	1·495	1·629	1·951	2·062
2·0	4·04	—	1·363	1·542	1·514	1·608	2·011	2·132
2·5	4·33	—	1·307	1·597	1·520	1·702	2·064	2·199
3·0	4·66	—	1·430	1·650	1·544	—	2·110	2·280
3·5	4·92	—	1·464	1·603	1·559	—	2·152	2·354
4·0	5·17	—	—	—	1·584	—	—	2·434
4·5	—	—	—	.	1·607	—	—	—

Accuracy: ±0·002

SUCROSE IN AQUEOUS SOLUTION AT 25 °C. (REFERENCE SUBSTANCE)

c	$D . 10^5$ cm.^{2}/sec.
0·146	0·510
0·708	0·499
0·468	0·479
0·902	0·416

Accurate to ±0·01

R. H. STOKES, *Thesis*, Cambridge, 1949.

TABLE III, 33

CONDUCTANCE OF SOME PERCHLORATES IN ORGANIC SOLVENTS AT 25 °C.

Values of the constants Λ_∞ and B in the equation

$$\Lambda_v = \Lambda_\infty - B\sqrt{c}$$

For Mg(ClO₄)₂ at 25 °C.			
Solvent	Λ_∞	B	
H_2O	128·5	244	
* $MeNO_2$	115·7	873	
* McOH	83·2	190	
* Me_2CO	185·5	2350	
n-PrOH	25·8	412	
i-PrOH	13·5	189	

Perchlorates in acetone at 25 °C.			
Salt	Λ_∞	B	
$Mg(ClO_4)_2$	185·5	2350	Theoretical limiting slopes not
$Ca(ClO_4)_2$	198·9	2817	in agreement with observed
$Ba(ClO_4)_2$	201·3	1603	B values.

P. VAN RYSSELBERGHE and R. M. FRISTROM, *J. Am. Chem. Soc.*, 1945, **67**, 680.

TABLE III, 34

CONDUCTANCE OF TETRA-METHYL-AMMONIUM SALTS IN ETHANOL AT 25 °C.

Constants of the equation $\Lambda_v = \Lambda_\infty - B\sqrt{c}$.

Values valid up to $\sqrt{c} = 0.04$.

Salt	Λ_∞	B	
(Me_4N) Cl	52·68	307	
(Me_4N) Br	55·10	338	
(Me_4N) CNS	58·45	340	
(Me_4N) NO_3	50·85	325	
(Me_4N) Picrate	55·68	282	

T. H. MEAD, O. M. HUGHES and H. HARTLEY, *J. Chem. Soc.*, 1933, 1207. See also
P. WALDEN, *Z. physik. Chem.*, 1931, **153**, 1.

TABLE III, 35

CONDUCTANCE OF HYDROGEN CHLORIDE IN DIOXAN WATER MIXTURES

(c in mol/l.; Λ_v = equivalent conductance)

15 °C.		25 °C.		35 °C.		45 °C.	
$\sqrt{c}$	Λ_v	$\sqrt{c}$	Λ_v	$\sqrt{c}$	Λ_v	$\sqrt{c}$	Λ_v
20% Dioxan							
0·01175	249·28	0·03661	297·68	0·02407	349·65	0·01061	405·28
0·01638	248·94	0·05198	295·56	0·03731	347·48	0·02918	401·02
0·04760	245·45	0·12353	287·01	0·05280	344·86	0·06620	393·30
0·10710	239·63	0·14518	285·02	0·10467	337·03	0·09012	387·08
0·15451	235·84	0·15854	283·08	0·14141	332·46	0·13701	381·56
0·17866	234·11	0·17329	282·19	0·16717	329·50	0·15917	378·13
0	250·7	0	302·7	0	354·2	0	406·0
45% Dioxan							
0·01400	144·99	0·01289	178·05	0·02345	211·79	0·01144	249·02
0·02749	142·74	0·03100	174·92	0·03964	208·59	0·02406	247·41
0·04172	140·86	0·04259	173·17	0·05505	205·86	0·05625	239·25
0·09701	134·68	0·09685	165·26	0·10784	196·16	0·10050	229·52
0·14148	130·04	0·12540	161·84	0·14669	190·91	0·11804	226·23
0·16344	129·39	0·16230	158·29	0·17403	187·84	0·13752	222·94
0	146·7	0	180·2	0	216·5	0	253·6
70% Dioxan							
0·00819	72·54	0·01160	89·14	0·00835	108·88	0·00930	126·08
0·02602	67·20	0·02888	81·45	0·02401	90·97	0·03046	112·51
0·05320	59·71	0·05079	78·43	0·05080	87·16	0·05707	98·10
0·10288	51·61	0·10421	62·05	0·07881	78·35	0·11000	82·54
0·14058	48·17	0·13990	57·94	0·10725	72·45	0·15090	76·27
0	74·5	0	93·1	0	112·4	0	131·9
82% Dioxan							
0·00819	38·53	0·01212	40·89	0·00563	58·01	0·00751	65·88
0·02077	28·31	0·02842	28·04	0·01322	45·63	0·02323	39·55
0·04769	18·86	0·05099	20·60	0·03239	29·53	0·04462	27·25
0·09304	13·87	0·10966	14·63	0·06916	19·72	0·09640	18·36
0·12698	12·49	0·14723	13·42	0·11014	16·14	0·13223	16·48
0	47·2	0	57·5	0	69·6	0	88·3

B. B. OWEN and G. W. WATERS, *J. Am. Chem. Soc.*, 1938, **60**, 2371.

TABLE III, 36

CONDUCTANCE OF SULPHURIC ACID IN METHANOL

Constants of the equation $\Lambda_v = \Lambda_\infty - B\sqrt{c}$

$$(\Lambda_v)_{20\,°C.} = 177\cdot2 - 491\cdot9\sqrt{c}$$
$$(\Lambda_v)_{30\,°C.} = 198\cdot8 - 592\cdot9\sqrt{c}$$
$$(\Lambda_v)_{35\,°C.} = 210\cdot0 - 677\cdot2\sqrt{c}$$

Equations valid up to $c = 2\cdot24 \cdot 10^{-3}$ molar.

Λ_v accurate to $\pm 0\cdot2\%$ assuming no error in $\sqrt{c}$.

E. W. KANNING, J. B. BYRNE and E. G. ROBALEK, *J. Am. Chem. Soc.*, 1944, **66**, 1700.

TABLE III, 37

CONDUCTANCE OF SULPHURIC ACID IN ETHER AT 0 °C. AND 25 °C.

$\varkappa_0$, $\varkappa_{25}$ = Specific conductance at 0 °C. or 25 °C.

H_2SO_4		at 0 °C.	at 25 °C.
vol. %	wt. %	$\varkappa_0 \cdot 10^4$ mho.cm.	$\varkappa_{25} \cdot 10^4$ mho.cm.
27·44	22·22	1·8	2·7
52·30	45·37	23	38
12·99	56·24	87	147
77·17	71·85	265	398
87·78	84·43	458	765
92·85	90·76	469	831
96·58	95·46	307	—
100	100	50	117

S. YCAHOBNY, *J. Gen. Chem. Russ.*, 1934, **14**, 215.

TABLE III, 38

CONDUCTANCE OF SALTS IN GLYCEROL AT 25 °C.

Λ_v' = molecular conductance at a dilution of V litre/mol.

Salt	V	Λ_v'	Salt	V	Λ_v'	Salt	V	Λ_v'
CaCl₂	1·051	1·297	BaCl₂	3·022	2·263	SrCl₂	2·472	1·474
	4·045	1·993		7·496	2·654		4·002	2·133
	8·053	2·51		15·45	3·028		7·980	2·528
	16·98	2·865		34·35	3·153		15·01	2·852

J. SZPER and Z. GAJEWSKI, *J. Chim. Phys.*, 1935, **32**, 705, and *Rocz. Chem.*, 1934, **24**, 570.

TABLE III, 39

CONDUCTANCE OF SALTS IN BENZENE AND DIOXAN

c in mol/l., Λ_y = equivalent conductance

AgClO$_4$ at 25 °C. in Benzene			
$c \cdot 10^4$	$\Lambda_y \cdot 10^5$	$c \cdot 10^2$	$\Lambda_y \cdot 10^4$
0·23	2·20	0·473	0·72
0·10	1·12	3·49	2·41
12·6	0·63	9·05	11·70
33·0	0·66	14·10	26·3

$\Lambda_\infty = 150$

Tetra-iso-amylammonium iodide at 60 °C. in Benzene			
$c \cdot 10^5$	$\Lambda_y \cdot 10^4$	$c \cdot 10^4$	$\Lambda_y \cdot 10^4$
3·01	6·49	0·88	6·22
14·20	4·21	6·88	16·8
43·3	4·06	28·2	23·3

$\Lambda_\infty = 155$

Tetra-butylammonium acetate at 25 °C. in Benzene			
$c \cdot 10^4$	$\Lambda_y \cdot 10^5$	$c \cdot 10^4$	$\Lambda_y \cdot 10^5$
0·1136	2·13	3·136	0·622
1·132	0·804	5·505	0·764
2·095	0·596		

$\Lambda_\infty = 100$

Tetra-butylammonium perchlorate at 25 °C. in Benzene			
$c \cdot 10^4$	$\Lambda_y \cdot 10^4$	$c \cdot 10^4$	$\Lambda_y \cdot 10^4$
0·00766	2·34	54·9	5·65
0·1216	1·23	129·4	13·30
1·125	2·10		
12·89	3·14		

$\Lambda_\infty = 100$

Tetra-butylammonium acetate at 25 °C. in Dioxan			
$c \cdot 10^5$	$\Lambda_y \cdot 10^5$	$c \cdot 10^5$	$\Lambda_y \cdot 10^5$
1·120	1·280	17·67	0·494
8·98	0·712	32·1	0·484
		45·8	0·515

$\Lambda_\infty = 51$

Tetra-butylammonium perchlorate at 25 °C. in Dioxan			
$c \cdot 10^4$	$\Lambda_y \cdot 10^4$	$c \cdot 10^4$	$\Lambda_y \cdot 10^4$
0·0294	1·24	5·58	1·64
0·1251	0·687	19·20	2·68
1·001	0·836	104·5	7·82

$\Lambda_\infty = 51$

R. M. Fuoss, C. A. Kraus and W. F. Luder, J. Am. Chem. Soc., 1936, 58, 255.

TABLE III, 40

CONDUCTANCE OF ELECTROLYTES IN ANHYDROUS LIQUID AMMONIA AT —40 °C.

V = dilution in litre/g. equiv.

Λ_v = equivalent conductance at dilution V.

NH₄NO₃				NH₄Cl			
V	Λ_v	V	Λ_v	V	Λ_v	V	Λ_v
9·39	106·02	333·6	187·5	10·08	62·8	345·6	148·1
19·51	115·37	699·1	209·55	20·98	72·38	730·7	177·9
40·58	129·26	1458	229·3	43·81	86·42	1546	206·1
86·57	147·88	3017	244·75	94·05	100·87	3225	231·9
182·8	169·78	6841	254·56	194·2	130·58	6824	250·0
388·0	198·84	19360	260·53	411·2	158·13	14471	263·4
827·5	216·4	28620	266·1	877·0	188·0	30294	270·6
1758	235·63	60780	270·4			63060	273·5

NaCl				NH₄Br			
V	Λ_v	V	Λ_v	V	Λ_v	V	Λ_v
74·31	124	49·85	112	2·93	86·03	49·63	126·8
166·2	149·9	111·5	135	6·23	91·07	108·5	148·2
379·7	179·5	255·2	163·4	13·34	100·1	236·9	173·3
860·5	210·4	579·3	194	28·07	112·6	517·1	199·2
1961·4	238·2	1322	222·0	50·99	130·05	1137	224
4430	260·1	3042	249·5	120·1	152·0	2464	243·6
10020	273·2	6906	268·5	272·5	177·0	5317	258·8
22740	282·6	15470	280	579·5	201·8	11410	270·0
50920	284	35090	285·2	1228	225·5	24920	270
		79070	287·7	2597	244·2	54150	278·8
				5550	259·2		
				11650	269·2		

NH₄ClO₄				KClO₄			
V	Λ_v	V	Λ_v	V	Λ_v	V	Λ_v
22·40	142	18·69	139·2	46·52	150·3	35·98	152·6
51·37	156·4	41·68	152·7	106·4	185·2	79·07	173·8
116·7	175·7	94·98	171·5	246·6	210·5	185·1	200·6
262·2	197·3	214·8	192·8	557·9	238·3	421·4	227·2
600·9	218·1	485·6	213·7	1241	262·5	953·7	253·6
1323	236	1108	231·5	2809	283·7	2187	273·9
2971	248·9	2526	245	6372	297·1	4826	289·6
6663	258	5773	250·7	14180	302	11010	298·5
15240	266·2	13020	263·9	31290	306·3	24490	304·2
33310	269·1	29150	267·0	68380	307	55370	305·7

TABLE III, 40 (*Continued*)

CH₃COOH				CH₃COONa			
V	Λ_v	V	Λ_v	V	Λ_v	V	Λ_v
4·12	11·25	29·51	16·55	101·3	28·9	107·8	30·48
9·32	12·45	67·52	22·3	225·8	40·1	240·9	41·45
21·59	15·17	154·5	30·9	522·8	50·3	547·7	57·78
48·91	19·85	354·1	43·4	1178	74·5	1259	81·8
111·5	27·17	803·1	60·7	2782	105·4	2844	107·8
257·9	38·18	1842	84·2	6121	136·0	6514	140·4
578·8	53·54	4185	113·1	13710	169·5	14020	173·4
1346	74·44	9596	148·7	30940	200·0	33370	202
3061	101·6	21840	183·9	71480	226·4	76340	229·7
6993	132·3	49890	210·5				
		112600	246·1				

CH₃COOK				HCOOH			
V	Λ_v	V	Λ_v	V	Λ_v	V	Λ_v
89·46	28·82	89·59	28·87	4·02	26·83	11·52	30·12
205·4	40·5	201·2	39·98	10·37	29·67	26·01	37·51
470·4	56·80	460·7	56·11	51·75	45·71	137·7	63·85
1072	79	1045	78·01	110·8	60·48	309·7	85·10
2432	108·2	2406	107·2	610·4	108·1	1598	144
5524	148·6	5513	180·6	1423	141·0	3600	180·7
12520	182·3	12470	180·6	3158	174·9	8431	213·6
28120	220·5	28040	218·5	7124	208·1	19060	237·9
64450	256·3	63020	253·1	16330	236·1	43480	255·2
				36940	252·3		
				84730	260·6		

HCOONa				C₂H₅COOH			
V	Λ_v	V	Λ_v	V	Λ_v	V	Λ_v
70·01	54·2	90·46	59·1	91·57	30·84	81·66	29·62
160·5	72·4	208·0	80·05	200·5	42·27	184·5	40·63
366·0	96·5	475·1	107·0	466·0	57·94	421·0	55·05
888·3	125·9	1087	139·3	1068	79·15	960·0	76·35
1889	160·5	2500	175·6	2458	105·15	2206	102
4239	193·9	5621	205·3	5634	135·1	5018	130·7
9648	224	13200	234·5	12860	160·5	11400	160·1
21560	245	29750	257·7	29500	191·7	26330	186·7
48800	262			66680	209·2	60440	206

TABLE III, 40 (*Continued*)

C_4H_9COONa				H_2S			
V	Λ_v	V	Λ_v	V	Λ_v	V	Λ_v
394	60·54	211·6	47·54	17·8	07·97	38·85	82·54
898·6	82·09	479·2	04·48	38·85	82·83	87·81	103·05
2071	109·2	1091	86·71	89·53	103·0	197·8	129·5
4718	139·0	2497	114·0	194·6	128·2	452·0	160·7
10500	168·1	5654	142·7	441·7	158·9	1030	194·4
24340	192·0	13050	171·4	985·3	190·2	2338	225·5
54190	208·0	20920	194·0	2204	220·1	5223	250·1
		66080	208·2	4981	243·8	11760	266·9
				11250	263·2	26500	273·1
				24800	208·7	59600	273·2
				50700	271·1		

HCN				$Sr(NO_3)_2$			
V	Λ_v	V	Λ_v	V	Λ_v	V	Λ_v
5·82	73·25	6·05	78·32	4·05	88·53	7·92	96·75
12·78	81·42	10·22	80·02	9·29	101·3	17·87	118·6
28·65	04·88	22·88	92·67	20·8	124·0	40·89	145·45
63·40	116·7	51·08	110·6	47·83	152·9	93·93	177·4
141·8	138·6	115·2	134·4	109·7	184·9	215·1	211·7
319·0	167·0	201·3	163·7	249·3	219·8	493·4	258·1
721·0	199·2	585·8	103	569·3	255·7	1132	299·9
1639·5	228·1	1300	222·3	1310	306·3	2502	356·3
3719	251·8	2951	244·8	3064	368	5946	423·3
8416	269·9	6587	201·7	6090	434·5	13580	487·8
18890	274·2	15040	275·6	15794	408·4		
42690	276·2	33400	277·6				

$Ba(NO_3)_2$				$Ca(NO_3)_2$			
V	Λ_v	V	Λ_v	V	Λ_v	V	Λ_v
150·3	113·1	77·03	93·12	123·1	106·3	21·65	70·63
359·9	139·1	173·5	114·5	278·7	131·1	48·47	88·56
816·6	168·8	382·5	139·9	628·4	161·5	108·0	101·0
1819	199·0	867·8	160·9	1438	194·4	247·2	120·8
4096	234·4	1940	201·6	3234	229·9	565·1	155·6
9292	273·8	4383	235·9	7212	270	1296	188·5
21100	324·5	9753	275	16090	317·9	2050	224·1
47870	384·3	22070	383·6	36790	379·2	6713	265·1
110300	452·6	49150	384·3	83090	447·2	15010	316·5
						35220	376·4
						72870	443·8

V. A. Pleskov, *Acta Physicochim. U.R.S.S.*, 1936, 5, 509. For older work see also C. A. Kraus and W. B. Bray, *J. Am. Soc. Chem.*, 1913, 35, 1335. Franklin and C. A. Kraus, *J. Am. Chem. Soc.*, 1900, 23, 287; *ibid.*, 1905, 27, 191; *Z. physik. Chem.*, 1909, 69, 272.

TABLE III, 41

CONDUCTANCE OF SALTS IN LIQUID SULPHUR DIOXIDE

Equivalent conductance at dilution V litre/g.equiv.

Compound	$V = 64$	$V = 128$	$V = 250$	$t\ °C.$
NaI	35·7	—	—	0
NH$_4$I	44·3	—	—	0
KI	48·3	57·7	—	0
RbI	53·0	63·0	—	0
KBr	—	48·8	—	—10
KSbCl$_6$	—	95·2	—	—12
NH$_4$SCN	10	—	—	0
(CH$_3$)$_3$SI	86·0	100·6	—	0
(CH$_3$)$_4$NCl	—	103·5	—	0
(CH$_3$)$_4$NBr	—	105·9	—	0
(CH$_3$)$_4$NI	—	111·5	—	—12
[(CH$_3$)$_4$N]$_2$SO$_4$	—	76·5	—	—12
[(CH$_3$)$_4$N]ClO$_4$	—	85	—	—12
[(CH$_3$. C$_2$H$_4$)$_3$C]ClO$_4$	—	—	113	0
[(CH$_3$. C$_6$H$_4$)$_3$C]Cl	—	—	128	0

G. JANDER and H. MESECH, Z. physik. Chem., 1939, 183 A, 255.

TABLE III, 42

CONDUCTANCE OF SALTS IN HYDROGEN CYANIDE

The following equations express the dependence of Λ_y upon $\sqrt{c}$ for values of $\sqrt{c}$ up to 0·04 (where c is in mol/l.) to an accuracy of $\pm 0·03\%$.

Salts	Constants in the equation $\Lambda_y = \Lambda_\infty - B\sqrt{c}$		Salts	Constants in the equation $\Lambda_y = \Lambda_\infty - B\sqrt{c}$	
	Λ_∞	B		Λ_∞	B
LiCl	345	335	NaClO$_4$	323·5	235
LiBr	346·0	270	NaCNS	333·7	230
LiI	348·0	258	Sodium Picrate	266·9	195
LiNO$_3$	336·6	402	KCl	361·4	280
LiClO$_4$	336·9	230	KBr	368·2	248
LiCNS	340·6	400	KI	363·9	235
NaBr	343·8	243	KNO$_3$	353·9	253
NaI	344·9	238	RbCl	363·2	195
NaNO$_3$	333·8	250	CsCl	368·2	200
			NEt$_4$Cl	282·8	195

J. E. COATES and E. G. TAYLOR, J. Chem. Soc., 1936, 1245.

See also J. E. COATES and E. G. TAYLOR, Nature, 1934, 134, 241.

TABLE III, 43

CONDUCTANCE OF ALKYL AMMONIUM CHLORIDES IN LIQUID HYDROGEN SULPHIDE AT —78·5 °C.

Concentration in mol/l.　　Λ_y = equivalent conductance.

Ethylammonium chloride		Diethylammonium chloride	
conc.	$\Lambda_y \cdot 10^4$	conc.	$\Lambda_y \cdot 10^2$
0·001073	1·56	0·0002032	19·8
0·004993	1·12	0·0003154	18·1
0·008065	0·740	0·0005182	8·89
		0·001465	6·94
		0·002023	6·04
		0·01127	3·91
		0·01996	3·86

Triethylammonium chloride		Tetrapropylammonium chloride	
conc.	$\Lambda_y \cdot 10^2$	conc.	Λ_y
0·0001556	12·6	0·0003434	7·29
0·001115	8·05	0·001556	4·01
0·004868	5·87	0·01086	3·23
0·009710	5·55	0·02573	4·69
0·0222	6·49	0·07463	8·64
0·1211	26·8		

Tetraethylammonium chloride		Tetramethylammonium chloride	
conc.	Λ_y	conc.	Λ_y
0·0004173	4·72	0·000837	2·22
0·001437	2·50	0·002479	2·14
0·002145	2·56	0·02556	1·47
0·02375	2·66	0·05786	2·58
0·05006	4·01	0·07994	3·14

E. E. LINEKEN and J. A. WILKINSON, *J. Am. Chem. Soc.*, 1940, **62**, 251.

TABLE III, 44

c in g.equiv./l.

Methanol
Equivalent conductance

Salt	Conc. t °C.	25·0	70·0	110·0	140·0	185·0	218·0
LiCl	$c = 0.814$	22·90	40·0	58·2	70·3	81·8	78·7
	$c = 0.2131$	40·5	68·9	94·5	109·3	110·1	88·1
	$c = 0.02044$	68·5	108·0	152·4	179·1	177·9	107·2
	$c = 0.001980$	83·4	142·1	210	265	317	225
LiBr	$c = 0.882$	25·10	45·1	66·5	81·2	100·4	108·9
	$c = 0.2244$	43·6	74·0	102·4	118·1	123·7	98·6
	$c = 0.01858$	69·6	117·8	168·0	201·4	216·6	146·2
	$c = 0.001910$	85·4	147·1	220	278	349	275
LiI	$c = 0.786$	28·20	50·6	73·9	92·1	113·0	127·3
	$c = 0.1822$	44·5	74·2	100·0	125·1	140·8	132·0
	$c = 0.01997$	59·0	98·0	139·8	171·3	197·0	150·7
	$c = 0.002557$	71·4	123·2	179	230	297	264
NaI	$c = 0.775$	39·5	69·6	99·7	119·3	140·5	149·7
	$c = 0.1024$	56·9	95·0	133·9	155·1	164·9	131·0
	$c = 0.01824$	80·4	135·7	191·6	228·5	249·1	159·7
	$c = 0.001899$	97·6	167·8	250	311	380	316
KI	$c = 0.494$	51·0	85·2	115·1	134·5	151·4	140·6
	$c = 0.2077$	62·2	100·1	134·5	151·4	157·0	127·6
	$c = 0.01069$	87·1	142·8	198·9	230·8	242·2	160·3
	$c = 0.001070$	105·2	178·1	260	329	395	314
CaI$_2$	$c = 0.906$	24·87	42·8	58·7	65·6	68·5	62·8
	$c = 0.1054$	41·4	63·4	77·6	77·1	62·2	37·1
	$c = 0.01110$	61·7	94·9	116·9	119·8	109·6	66·5
	$c = 0.001161$	82·4	135	178	192	185	187
i-(C$_5$H$_{11}$)$_4$NI	$c = 0.1832$	37·59	67·3	98·0	121·5	144·3	146·4
	$c = 0.02096$	67·3	113·4	163·0	195·0	227·8	194·5
	$c = 0.001866$	94·2	158·9	233	292	375	296

P. C. BLOKKER, *Rec. Trav. Chim.*, 1935, **54**, 975.

TABLE III, 44 *(Continued)*

Acetone
Equivalent conductance

Salt	Conc.	*t* °C.	25·0	70·0	110·0	140·0	185·0	215·0
LiCl	$c = 0.0600$		4·90	5·14	8·94	2·34	—	—
	$c = 0.00999$		12·06	12·36	11·2	9·3	6·2	2·7
LiBr	$c = 0.802$		0·17	8·92	10·17	10·45	10·45	10·09
	$c = 0.1752$		12·86	15·23	15·10	13·67	10·35	7·23
	$c = 0.01717$		30·7	35·7	33·0	27·37	17·93	30·6
	$c = 0.002007$		70·4	84·3	79·8	67·0	43·2	21·9
LiI	$c = 0.802$		17·04	26·20	33·6	37·7	40·3	42·8
	$c = 0.2004$		31·1	42·6	49·0	49·4	42·2	33·1
	$c = 0.01978$		64·3	85·1	93·2	90·0	68·4	45·0
	$c = 0.001972$		106·2	140·4	167·4	172·8	125·8	74·0
NaI	$c = 0.448$		42·1	44·4	41·4	35·8	—	—
	$c = 0.1594$		59·1	61·3	54·3	44·2	—	—
	$c = 0.01438$		104·7	120·2	127·9	106·2	61·2	32·7
	$c = 0.002016$		144·0	184·3	190·9	180·8	127·8	68·5
KI	$c = 0.01478$		105·2	120·8	110·1	99·0	—	—
	$c = 0.000330$		176·9	237	279	299	240	150
CaI$_2$	$c = 0.983$		77·5	106·6	125·6	129·3	—	—
	$c = 0.2544$		121·9	145·0	148·6	135·5	117·3	93·8
	$c = 0.02520$		271·6	310	308	263·7	193·8	146·1
	$c = 0.002494$		527	656	693	663	506	376
i-(C$_5$H$_{11}$)$_4$NI	$c = 0.1702$		30·8	40·3	47·3	51·3	—	—
	$c = 0.01913$		64·1	81·6	91·8	93·9	—	—
	$c = 0.001907$		98·1	131·3	155·2	168·1	—	—

P. C. BLOKKER, *Rec. Trav. Chim.*, 1935, **54**, 975.

TABLE III, 45

IONIC MOBILITIES (l_∞) AT INFINITE DILUTION FOR METHANOL AND ETHANOL

	Methanol		Ethanol	
Ion	(25 °C.)	(4 °C.)	(25 °C.)	(4 °C.)
H'	141·8	118·2	57·40	37·24
Li'	—	·--	15·00	9·02
K'	53·6	39·35	—	—
Hg$_2$''	49·7	36·6	20·95	13·53
Me$_4$N'	70·10 *	—	28·3 *	—
Et$_4$N'	61·5	46·65	27·85	18·75
Cl'	51·27	37·12	24·30	16·01
Br'	56·4	41·85	—	—
I'	—	—	28·80	19·30
ClO$_4$'	70·1	52·85	88·55	22·40
NO$_3$'	60·5	45·2	—	—
OMe'	53·02	36·76	—	—
OEt'	—	—	25·35	16·01
MeCO$_3$'	44·7	32·65	—	—
EtCO$_3$'	—	—	21·15	14·27
Picrate	46·5	34·1	26·30	17·55

l_∞ values accurate to 0·5 - 1%

A. G. OGSTON, *Trans. Faraday Soc.*, 1936, **32**, 1679.

* T. H. MEAD, O. M. HUGHES and H. HARTLEY, *J. Chem. Soc.*, 1933, 1207.

TABLE III, 46

IONIC MOBILITIES l_∞ AT INFINITE DILUTION IN ETHANOL WATER MIXTURES AT 25 °C.*

Mol % EtOH	Picrate	Li'	Mol % EtOH	Cl'
5	21·7	26·7	2·17	60·2
10	16·5	19·9	10·83	34·2
15	14·1	16·7	17·19	28·2
20	13·4	15·2	46·87	23·2
30	13·6	14·0	93·55	22·4
40	14·4	13·8		
60	17·6	14·7		
80	21·8	15·6		

TABLE III, 46 (*Continued*)

Mol % EtOH	Sr''	Br'	Mol % EtOH	H'
2·02	58·6	—	40	75·9 †
8·90	85·1	—	72·9	29·2
20·68	24·1	27·8	87·3	28·6
30·97	20·5	25·00	92·2	28·1
61·00	18·8	—	96·0	22·8
			99·0	31·4
			99·8	48·4
l_∞ values accurate to 0·5 - 1%.			100	61·3

* A. WELLER, *Dissertation*, Tübingen, 1950.
† J. J. HERMANS, *Rec. Trav. Chim.*, 1937, 56, 658.

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I. S. BIGICH, *J. Gen. Chem. Russ.*, 1946, 16, 1783.

TABLE III, 47

CATION TRANSFERENCE NUMBER IN AQUEOUS SOLUTIONS AT 25 °C.

The values of (n_+) calculated by equation (1) below, require that the concentration be expressed in mol/l. If the data are plotted against the square root of the equivalent concentration, the limiting slopes become -0.18508, $+0.0447$, $+0.1048$ and -0.3170 for $CaCl_2$, Na_2SO_4, K_2SO_4 and $LaCl_3$ respectively.

n_+ may be expressed as $f(c)$ by the equation:

$$+ S_{(n_+)} \sqrt{c} \qquad (1)$$

for high dilutions, or in general by the equation:

$$n_+ = n_{+\infty} + S_{(n_+)} \sqrt{c} \cdot \frac{\Lambda_\infty}{\Lambda_y},$$

where Λ_y is a calculated value.

Electrolyte	Ref.	Λ_∞	$S_{(n_+)}$ see eqn. (1)	$n_{+\infty}$	Concn. (g. equiv./litre)				
					0·01	0·02	0·05	0·10	0·20
HCl	(¹)	426·17	+ 0·04507	0·8209	0·8251	0·8266	0·8292	0·8314	0·8337
Na Acetate	(²)	90·99	+ ·08336	·5507	·5537	·5550	·5573	·5594	·5610
K Acetate	(⁶)	114·40	+ ·07467	·6427	·6498	·6523	·6560	·6609	—
KNO₃	(²)	144·96	+ ·00297	·5072	·5084	·5087	·5093	·5103	·5120
NH₄Cl	(²)	149·94	— ·00363	·4909	·4907	·4906	·4905	·4907	·4911
KCl	(¹)	149·86	— ·00376	·4906	·4902	·4901	·4899	·4898	·4894
KI	(²)	150·29	— ·00430	·4892	·4884	·4883	·4882	·4883	·4887
KBr	(²)	151·63	— ·00596	·4849	·4833	·4832	·4831	·4833	·4841
AgNO₃	(²)	133·36	— ·01604	·4643	·4648	·4652	·4664	·4682	—
NaCl	(¹)	126·48	— ·04910	·3963	·3918	·3902	·3876	·3854	·3821
LiCl	(¹)	115·03	— ·08514	·3304	·3289	·3261	·3211	·3168	·3112
CaCl₂	(³)	135·84	— ·26174	·4380	·4204	·4220	·4140	·4060	·3953
Na₂SO₄	(³)	129·9	+ ·0032	·386	·3848	·3836	·3829	·3828	·3828
K₂SO₄	(⁴)	153·3	+ ·1482	·479	·4829	·4848	·4870	·4890	·4910
LaCl₃	(⁵)	145·9	— ·5491	·477	·4625	·4576	·4482	·4375	·4233
K₄Fe(CN)₆	(⁷)	—	—	—	·515	·555	·604	·647	—
K₃Fe(CN)₆	(⁷)	—	—	—	—	—	·475	·491	—

Accuracy: $\pm 0.02\%$

References:

1 L. G. LONGSWORTH, *J. Am. Chem. Soc.*, 1932, 54, 2741.

2 L. G. LONGSWORTH, *ibid.*, 1935, 57, 1185.

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6 D. J. LE ROY and A. R. GORDON, *J. Chem. Phys.*, 1938, 6, 398.

7 G. PRIDEAUX, *J. Chem. Soc.*, 1944, 606.

See also vol. I, Table 2, p. 88.

TABLE III, 48

CATION TRANSFERENCE NUMBERS FOR HIGHER CONCENTRATIONS OF ELECTROLYTES
IN AQUEOUS SOLUTIONS AT 25 °C.

(c in g.mol/l.)

1. ZnI$_2$ [1]		2. Zn(ClO$_4$)$_2$ [2]		3. ZnCl$_2$ [2]	
c	n_+	c	n_+	c	n_+
0·05	0·382	0·1	0·409	0·3271	0·333
0·1	0·363	0·2	0·397	0·1344	0·342
0·3	0·332	0·3	0·389	0·0500	0·365
0·6	0·317	0·4	0·377	0·0210	0·379
1·0	0·291	0·5	0·368	0·0097	0·390
2·5	0·115	0·7	0·349		

4. ZnBr$_2$ [2]	
c	n_+

3·0	0·056	1·0	0·335		
4·0	—0·050 *	1·5	0·317	0·3291	0·341
5·0	—0·190 *	2·0	0·303	0·1011	0·368
8·0	—0·444 *	3·0	0·281	0·0499	0·384
10·0	—0·550 *	4·0	0·271	0·0201	0·398
				0·0119	0·402

Accuracy: ±0·002
* Complex formation

Accuracy: ±0·002

5. NaCl and KCl [4]

c	n_+ (NaCl)	n_+ (KCl)	c	n_+ (NaCl)	n_+ (KCl)
0	0·4437	0·5068	0·007	0·4413	0·5075
0·0005	0·4428	0·5069	0·01	0·4412	0·5077
0·001	0·4425	0·5070	0·02	0·4412	0·5085
0·002	0·4421	0·5071	0·03	0·4408	0·5092
0·003	0·4418	0·5072	0·05	0·4398	0·5105
0·005	0·4415	0·5074	0·08	0·4388	0·5114

Accuracy: ±0·0005

References:
[1] R. H. STOKES and B. J. LEVIEN, *J. Am. Chem. Soc.*, 1946, **68**, 1852.
[2] R. H. STOKES and B. J. LEVIEN, *J. Am. Chem. Soc.*, 1946, **68**, 333.
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[4] L. W. SHEMILT, J. A. DAVIES and A. R. GORDON, *J. Chem. Phys.*, 1948, **16**, 342.

TABLE III, 48 (*Continued*)

6. CaCl$_2$ ([5])				7. MgCl$_2$ ([6])	
c	n_+ (15°C.)	n_+ (25°C.)	n_+ (35°C.)	c	n_+
0	0·4334	0·4380	0·4427	0	0·395
0·005	0·4261	0·4307	0·4354	0·0032	0·396
0·01	0·4231	0·4277	0·4424	0·0088	0·404
0·02	0·4188	0·4234	0·4281	0·0073	0·391
0·03	0·4158	0·4204	0·4249	0·017	0·380
0·05	0·4105	0·4151	0·4198	0·028	0·380
0·07	0·4067	0·4113	0·4160	0·036	0·376
0·10	0·4024	0·4070	0·4117	0·052	0·375
0·15	0·3964	0·4010	0·4057		

Accuracy: $\pm 0\cdot 0002$

References:

[5] A. G. KEENAN, H. G. McLEOD and A. R. GORDON, *J. Chem. Phys.*, 1945, 13, 466.
[6] C. DRUCKER, *Rec. Trav. Chim.*, 1932, 51, 574.

TABLE III, 49

CATION TRANSFERENCE NUMBERS OF ELECTROLYTES IN NON-AQUEOUS SOLUTIONS

NaOAc and NH$_4$OAc in Anhydrous Acetic Acid at 25 °C. [1]			
NH$_4$OAc		NaOAc	
Molality	n_+	Molality	n_+
0·1923	0·520	0·3480	0·48
0·3003	0·500	0·5578	0·45
0·5214	0·486	0·7093	0·43
0·9750	0·478	0·8869	0·39
1·4455	0·469		
2·4298	0·449		

Accuracy: $\pm 0\cdot 02$

Values are obtained by the HITTORF method and agree with those obtained by the moving boundary method.

TABLE III, 49 (*Continued*)

	wt.% MgCl$_2$	n_+	wt.% MgCl$_2$. 6H$_2$O	n_+
MeOH	1·93	0·405	6·2	0·387
	10·6	0·399	8·0	0·385
EtOH	0·57	0·371	2·1	0·480
			6·93	0·469

Values obtained by Hittorf method.

	wt.%	n_+	Temperature °C.
NaI	2·812	0·386	18·8
LiBr	2·136	0·107	19·5
LiCl	1·0737	--0·210	14·5
	0·7513	—0·100	14·5

N.B.   No concentration dependence of t_+ is given in this work.

AgNO$_3$, KI, NaI in Ethanol at 25 °C. [4]

AgNO$_3$	$n_{+\infty} = 0.39$	
KI	$n_{+\infty} = 0.56$	Accuracy: ± 0.01
NaI	$n_{+\infty} = 0.005$	

References:
[1] W. C. LANNING and A. W. DAVIDSON, *J. Am. Chem. Soc.*, 1938, **61**, 147.
[2] F. OLMER, *Bull. Soc. Chim.*, 1938, (v) 5, 1685.
[3] W. BIRKENSTOCK, *Z. physik. Chem.*, 1928, **129**, 432.
[4] J. W. WOOLCOCK, H. HARTLEY and O. L. HUGHES, *Phil. Mag.*, 1931, (vii) 11, 222.

TABLE III, 50

TRANSFERENCE NUMBER $n_{+\infty}$ OF Li picrate AT INFINITE DILUTION IN ETHANOL-WATER MIXTURES AT 25 °C.[5]

Mol% EtOH	$n_{+\infty}$		Mol% EtOH	$n_{+\infty}$	
0	0,555		30	0,507	
5	0,550		40	0,489	
10	0,546	$\pm 0,5 - 1\%$	60	0,455	$\pm 0,5 - 1\%$
15	0,542		80	0,422	
20	0,530		100	0,390	

A. WELLER, *Dissertation*, Tübingen, 1950.

TABLE III, 51

TRANSFERENCE NUMBERS OF THE HYDROGEN ION IN NON-AQUEOUS SOLVENTS AT 25 °C.

HCl in aqueous-non-aqueous solvent mixtures. (0·01/0·1N HCl concentration-cell-
e.m.f. determination [1])

EtOH – H_2O mixtures		Me . CO . Me – H_2O mixt.		Glycerol – H_2O mixtures	
wt.% EtOH	n_+	wt.% Me_2CO	n_+	wt.% Glycerol	n_+
16·18	0·835	15·80	0·886	23·50	0·840
32·35	0·849	33·32	0·815	47·96	0·850
52·35	0·818	49·07	0·712	81·82	0·876
68·67	0·741	66·54	0·491	94·60	0·902
100	0·540	100	0·220	100	0·760

Mannitol – H_2O.		Chloral hydrate – H_2O		Glucose – H_2O	
wt.% Mannitol	n_+	wt.% $CCl_3 . CHO . 2H_2O$	n_+	wt.% Sugar	n_+
7·06	0·851	14·99	0·835	15·02	0·807
14·06	0·841	30·98	0·846	31·04	0·718

H_2SO_4 in anhydrous methanol at 25 °C. [2]

Molality	n_+	Molality	n_+
0·54484	0·742	0·07151	0·727
0·27714	0·734	0·02522	0·725
0·14118	0·729	0·01375	0·726

Accuracy probably: ±0·001
Values obtained by e.m.f. method (cf. 1).

References:
[1] T. ERDEY-GRUZ, Z. *physik. Chem.*, 1927, **131**, 87.
[2] E. W. KANNING and J. E. WALTZ, *J. Am. Chem. Soc.*, 1941, **63**, 2076.

See also data in Table III, 52 for HCl in dioxan-H_2O mixtures.

TABLE III, 52

CATION TRANSFERENCE NUMBERS OF HYDROGEN CHLORIDE IN WATER AND DIOXAN–WATER MIXTURES

X = wt.% Dioxan.

$X = 0$

m	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°
0·0	—	0·842	0·837	0·831	0·826	0·821	0·816	0·811	0·806	0·801	0·796
0·005	—	·844	·840	·834	·829	·824	·819	·814	·809	·804	·799
·01	—	·845	·841	·835	·830	·825	·821	·810	·811	·806	·801
·02	—	·846	·842	·836	·832	·827	·822	·818	·813	·808	·803
·05	—	·848	·844	·838	·834	·830	·825	·821	·816	·811	·806
·1	—	·850	·846	·840	·837	·832	·828	·823	·810	·814	·810
·2	—	·851	·847	·843	·830	·835	·830	·827	·828	·818	·814
·5	—	·854	·850	·846	·842	·838	·834	·831	·827	·822	·819
1·0	—	·855	·852	·848	·844	·841	·837	·833	·829	·824	·821
1·5	—	·857	·853	·849	·845	·842	·839	·835	·830	·825	·822
2·0	—	·857	·853	·849	·846	·843	·839	·835	·831	·826	·822
3·0	—	·858	·854	·850	·846	·843	·840	·836	·832	·827	·828

$X = 20$

m	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°
0·0	0·856	0·851	0·846	0·841	0·836	0·831	0·825	0·821	0·816	0·810	0·805
·005	·861	·855	·850	·845	·840	·835	·829	·825	·820	·814	·809
·01	·862	·857	·851	·846	·841	·836	·831	·827	·821	·816	·811
·02	·865	·859	·853	·848	·843	·838	·833	·829	·824	·818	·813
·05	·867	·861	·856	·851	·846	·841	·837	·832	·827	·822	·816
·1	·868	·862	·857	·852	·848	·843	·839	·834	·829	·823	·818
·2	·869	·863	·858	·853	·849	·844	·840	·835	·830	·825	·820
·5	·867	·862	·857	·852	·847	·843	·838	·833	·820	·823	·818
1·0	·864	·860	·854	·840	·844	·840	·836	·831	·826	·821	·810
1·5	·862	·857	·852	·847	·842	·838	·834	·829	·824	·819	·814
2·0	·860	·855	·850	·845	·841	·836	·832	·828	·823	·818	·813
3·0	·856	·852	·847	·842	·838	·833	·829	·825	·820	·816	·811

$X = 45$

m	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°
0·0	0·828	0·824	0·820	0·816	0·811	0·806	0·801	0·796	0·791	0·787	0·783
0·005	·833	·829	·825	·821	·816	·811	·807	·801	·797	·793	·788
·01	·835	·830	·827	·823	·818	·813	·809	·804	·799	·795	·790
·02	·838	·833	·829	·825	·820	·816	·811	·807	·802	·798	·793
·05	·842	·837	·833	·829	·824	·820	·816	·812	·807	·803	·798
·1	·845	·840	·836	·831	·827	·823	·819	·816	·811	·807	·803
·2	·849	·844	·840	·834	·830	·826	·823	·820	·816	·812	·807
·5	·851	·846	·842	·836	·833	·829	·826	·822	·819	·815	·811
1·0	·851	·846	·841	·836	·832	·828	·825	·822	·819	·815	·811
1·5	·850	·845	·840	·835	·832	·828	·824	·821	·818	·814	·810
2·0	·849	·844	·839	·835	·831	·827	·824	·820	·817	·813	·809
3·0	·847	·843	·838	·833	·830	·825	·822	·817	·814	·810	·807

TABLE III, 52 (*Continued*)

					$X = 70$						
m	0°	5°	10°	15°	20°	25°	30°	35°	40°	45°	50°
0·0	—	0·772	0·768	0·764	0·760	0·755	0·750	0·746	0·742	0·738	0·734
·005	—	·781	·778	·774	·770	·766	·761	·757	·753	·750	·747
·01	—	·783	·780	·777	·773	·769	·764	·760	·756	·753	·751
·02	—	·786	·783	·779	·776	·772	·767	·763	·760	·757	·755
·05	—	·788	·785	·782	·778	·774	·770	·766	·763	·760	·758
·1	—	·789	·786	·783	·780	·775	·771	·768	·765	·762	·759
·2	—	·789	·786	·784	·780	·776	·771	·768	·765	·762	·759
·5	—	·789	·786	·783	·779	·774	·770	·766	·764	·760	·757
1·0	—	·788	·785	·782	·777	·772	·768	·764	·762	·758	·754
1·5	—	·788	·784	·781	·776	·771	·766	·763	·760	·757	·752

					$X = 82$						
0·0	—	0·677	0·675	0·673	0·672	0·670	0·668	0·667	0·665	0·663	
·05	—	·742	·735	·730	·726	·722	·717	·712	·708	·702	
·1	—	·767	·764	·762	·759	·756	·754	·752	·750	·747	
·2	—	·755	·751	·747	·744	·740	·738	·735	·732	·729	
·3	—	·718	·715	·711	·708	·705	·702	·699	·696	·693	
·5	—	·660	·657	·654	·651	·648	·645	·642	·639	·637	

Accuracy: Uncertainties in the third decimal place for H_2O, 20%, 45% and 70% dioxan in H_2O, are respectively ± 3, ± 7, ± 4 and ± 8.

H. S. HARNED and E. C. DREBY, *J. Am. Chem. Soc.*, 1939, 61, 3113.

TABLE III, 53

EQUIVALENT CONDUCTANCE OF COLLOIDAL ELECTROLYTES AT 25 °C.

c in g.equiv./l.

Methyl Orange		Meta-Benzopurpurine		Congo Red	
$\sqrt{c} . 10^3$	Λ_v	$\sqrt{c} . 10^3$	Λ_v	$\sqrt{c} . 10^3$	Λ_v
9·24	69·3	8·96	77·8	6·22	82·4
6·52	69·8	5·45	85·4	2·65	99·7
4·98	70·3	4·01	88·6	1·90	101·6
4·12	68·4	6·39	84·2	1·40	103·7
3·36	70·8	2·71	91·7	0·928	104·5
1·80	71·5	1·52	91·2	0·658	103·9
0·726	71·7	0·70	88·1	0·405	103·4
		0·37	84·1	0·332	98·2
				0·287	96·3

TABLE III, 53 (Continued)

Benzopurpurine 4B		MC.1*		MC.8*	
6·30	86·1	6·34	67·9	3·00	70·5
5·21	89·3	1·03	70·3	1·35	100·6
3·68	94·0	1·45	70·3	1·04	110·7
2·33	98·2	0·84	70·5	0·77	122·0
1·64	99·3	0·56	71·0	0·57	130·9
1·093	99·6	0·37	72·6	0·40	134·8
0·414	99·3	0·20	73·9	0·26	141·0
0·295	98.5				

Accuracy of Λ values: $\pm 0\cdot 3\%$

From C. ROBINSON and H. E. GARRET, *Trans. Faraday Soc.*, 1939, **35**, 775.

* See C. ROBINSON and H. E. GARRETT, *loc. cit.*

EQUIVALENT CONDUCTANCE OF COLLOIDAL ELECTROLYTES AT 25 °C.

Na dodecyl sulphate (1)		Cetyl Pyridinium sulphate (1)	
Conc. mol/l.	Λ_y	Conc. mol/l.	Λ_y
0·002	80	0·0005	98
0·005	77	0·0008	98
0·008	76	0·001	93
0·010	63	0·002	79
0·015	40	0·003	72
0·020	43		
Cetyl pyridinium Bromide (2)		**Na Oleate (2)**	
0·00040	118	0·005	50
0·00087	107·1	0·0075	44
0·00121	86·9	0·01	39
0·00247	60·3	0·02	34
0·00499	46·5	0·03	30
0·0138	35·8		
0·1090	29·1		

Accuracy: $\pm 0\cdot 5\%$

(1) H. G. SCHMID and E. C. LARSON, Z. *Elektrochem.*, 1938, **44**, 651.

TABLE III, 53 (Continued)

Cetyl-trimethylammonium Bromide (2)		Potassium Oleate (2)	
g./l.	Λ_y (85 °C.)	Normality	Λ_y
0·00088	120·2	0·25	34·0
0·00080	118	0·5	37·0
0·00236	07·8		
0·00868	40·5	Potassium Laurate (2)	
0·0534	29·5		
0·128	28·3	0·20	41·8
0·421	27·7	1·0	47·1

Cetane Sulphonic Acid (2)		Sodium Oleate (2)	
Normality	Λ		
0·018 N	146	0·2	19·8
0·046	135	0·4	20·8
0·078	148	0·5	21·2
0·102	159	0·6	21·7

Accuracy: Λ values $\pm 0.5\%$
(2) G. S. HARTLEY, B. COLLIE and C. S. SAMIS, *Trans. Faraday Soc.*, 1936, **32**, 799.

TABLE III, 54

IONIC PRODUCT OF WATER (P)

$-\log_{10} P$	Temp. °C.	$-\log_{10} P$	Temp. °C.
14·9435	0	13·6801	35
14·7338	5	13·5348	40
14·5346	10	13·3960	45
14·3463	15	13·2617	50
14·1669	20	13·1369	55
13·9965	25	13·0171	60
13·8330	30		

Accurate to ± 0.0007

H. S. HARNED and R. A. ROBINSON, *Trans Faraday Soc.*, 1940, **36**, 977.
For earlier work see also:
[1] A. HEYDWEILLER, *Ann. Physik.*, 1909, **28**, 503.
[2] F. KOHLRAUSCH and A. HEYDWEILLER, *Ann. Physik*, 1894, **53**, 209.
[3] C. W. KANOLT, *J. Am. Chem. Soc.*, 1907, **29**, 1402.
[4] A. A. NOYES *et al.*, *J. Am. Chem. Soc.*, 1910, **32**, 159.
[5] H. LUNDEN, *J. Chim. Phys.*, 1907, **5**, 574.
For other solvents, see under dissociation constants of weak electrolytes.
See also vol. I, Table 27, p. 228.

TABLE III, 55

CONDUCTANCE OF FUSED SALTS

$$\varkappa = a + b \cdot 10^{-3} \, (t - t_1)$$

Substance	a (mho.cm.$^{-1}$)	b (mho.cm.$^{-1}$°C.$^{-1}$)	t_1 °C.
LiF	20·3	100	905
LiCl	7·59	1·0	780
NaF	3·15	8·3	1000
NaCl	3·66	2·2	850
KF	4·14	4·5	860
KCl	2·19	2·1	800
KBr	1·66	2·0	700
KI	1·35	2·3	710
RbCl	1·49	2·1	733
CsCl	1·14	2·0	660
CuCl	3·27	2·45	430
CuI	1·82	1·78	605
AgCl	4·44	1·84	600
AgBr	3·39	1·70	600
AgI	2·17	0·61	600
BeCl$_2$	0·0032	26	451
MgCl$_2$	1·05	1·7	729
KCl.MgCl$_2$	0·93	2·1	570
CaCl$_2$	1·99	3·5	705
SnCl$_2$	1·98	2·9	900
BaCl$_2$	1·71	3·0	900
ZnCl$_2$	0·051	1·5	460
CdCl$_2$	1·93	2·0	576
CdBr$_2$	1·06	2·0	571
CdI$_2$	0·19	2·1	389
Hg$_2$Cl$_2$	1·00	1·8	529
HgCl$_2$	0·00052	0·0005	294
AlCl$_3$	0·56 . 10^{-3}	—	—
AlCl$_3$.NH$_3$	0·0143	0·26	136
ScCl$_3$	0·56	2·8	959
YCl$_3$	0·40	2·0	714
LaCl$_3$	1·14	8·8	868
PrCl$_3$	0·90	3·7	824
NdCl$_3$	0·09	2·8	775
InCl$_3$	0·42	9·0	594
InCl$_2$	0·47	2·0	356
InCl	0·97	0·4	242

TABLE III, 55 (*Continued*)

Substance	a (mho.cm.$^{-1}$)	b (mho.cm.$^{-1}$ °C.$^{-1}$)	t_1 °C.
TlCl	1·17	8·5	450
ThCl$_4$	0·67	1·8	814
SnCl$_2$	0·89	5·7	263
PbCl$_2$	1·48	4·0	508
BiCl$_3$	0·44	1·4	266
MoCl$_5$	1·8 . 10^{-1}	—	—
Na$_2$MoO$_4$	1·41	1·75	843
WCl$_6$	1·9 . 10^{-1}	—	280
WCl$_5$	0·67	2·3	250
Na$_2$WO$_4$	1·001	1·82	752
UCl$_4$	0·34	2·8	570
TeCl$_4$	0·12	1·1	236

Accuracy: No statement is made. Accuracy (*cf.* Table III, 58) is probably of order ±5% for low melting compounds and is less satisfactory for those of higher melting points.

P. DROSSBACH, *Electrochemistry of Molten Salts*, Berlin, 1938.

See also vol. I, Table 13, p. 145.

TABLE III, 56

ENERGY OF ACTIVATION FOR CONDUCTANCE OF FUSED SALTS

$$\varkappa = A \, e^{-E/RT}$$

$$\Lambda_v = A' \, e^{-E'/RT}$$

$$\eta = \text{const.} \, . \, e^{B/RT}, \quad \Lambda_v = \frac{\varkappa E}{d}, \quad \varrho = \text{density}.$$

$E =$ Equivalent weight.

Salt	Λ_v	E in k.cal.	E' in k.cal.	B in k.cal.	A mho.cm.$^{-1}$
LiCl	188	1·15	1·72	8·8	11·5
NaCl	150	1·54	2·70	9·4	7·8
KCl	120	2·30	3·26	7·8	6·5
RbCl	94	2·83	3·66	—	6·5
CsCl	86	3·83	3·75	—	6·6

TABLE III, 56 (*Continued*)

Salt	Λ_ν	E in k.cal.	E' in k.cal.	B in k.cal.	A mho.cm.$^{-1}$
LiBr	177	1·75	—	6·0	13·5
NaBr	148	1·84	2·51	10·6	7·4
KBr	109	2·55	3·42	7·9	5·8
NaI	150	1·25	2·00	7·4	4·8
KI	104	2·75	3·70	9·2	5·5
AgCl	118	0·99	1·20	5·3	7·4
AgBr	99	0·70–1·00	0·90	4·5–5·4	—
AgI	105	0·80	0·90	5·8	4·0
CuCl	94	0·85	1·06	5·5	6·2
MgCl$_2$	85	3·56	3·97	—	6·4
CaCl$_2$	64	4·10	4·72	9·5	13·5
SrCl$_2$	69	4·00	4·65	—	11·0
BaCl$_2$	77	4·15	4·35	—	10·5
CdCl$_2$	58·5	2·30	2·18	4·5	7·8
CdBr$_2$	41·2	2·75	—	—	5·4
PbCl$_2$	58·0	2·3–4·5	4·20	6·6	—
PbBr$_2$	27	4·35	4·32	9·2	16·0

Accuracy of Λ_ν is $\pm 0.2\%$. Temperature coefficient data from which E and E' are derived is accurate to $\pm 0.2\%$. Accuracy of E and E' is of the order of $\pm 0.4\%$.
H. Bloom and E. Heymann, *Proc. Roy. Soc.*, 1947, **188A**, 392.

TABLE III, 57

THERMODYNAMIC DISSOCIATION CONSTANTS OF ACIDS IN AQUEOUS SOLUTION AT 25 °C.

Acid	$K_A \cdot 10^5$	Ref.	Acid	$K_A \cdot 10^5$	Ref.
Acetic	1·753	[1]	p-Fluorobenzoic	7·22	[7]
Monochloracetic	139·6	[2]	Phenylacetic	4·88	[8]
Propionic	1·343	[3]	o-Chlorophenylacetic	8·60	[8]
n-Butyric	1·506	[3]	m-Chlorophenylacetic	7·24	[8]
Benzoic	6·30	[4,5]	p-Chlorophenylacetic	6·45	[8]
o-Chlorobenzoic	119·7	[5]	o-Bromophenylacetic	8·84	[8]
m-Chlorobenzoic	15·06	[5]	p-Bromophenylacetic	6·49	[8]
p-Chlorobenzoic	10·4	[5]	p-Methoxyphenylacetic	4·36	[8]
o-Bromobenzoic	140	[7]	p-Iodophenylacetic	6·64	[8]
p-Bromobenzoic	10·7	[7]	Acrylic	5·50	[9]

TABLE III, 57 (*Continued*)

Acid	$K_A \cdot 10^5$	Ref.	Acid	$K_A \cdot 10^5$	Ref.
Lactic	13·87	[10]	Diethylmalonic	70·8	[13]
Carbonic	0·0431	[11]	Ethyl-*n*-propylmalonic	78·4	[13]
Malonic	139·7	[12]	Di-*n*-propylmalonic	92·0	[13]
Succinic	6·63	[12]	Phenylmalonic	277	[14]
Glutaric	4·54	[12]	Cyclopropane-1,1-di-		
Adipic	3·72	[12]	carboxylic	150	[15]
Pimelic	3·10	[12]	Cyclobutane-1,1-di-		
Suberic	2·99	[12]	carboxylic	7·55	[15]
Methylmalonic	8·47	[13]	Cyclopentane-1,1-di-		
Ethylmalonic	10·9	[13]	carboxylic	5·96	[15]
n-Propylmalonic	10·3	[13]	Cyclohexane-1,1-di-		
Dimethylmalonic	7·06	[13]	carboxylic	3·54	[15]
Methylethylmalonic	15·4	[13]			

References:

[1] D. A. MacInnes and T. Shedlovsky, *J. Am. Chem. Soc.*, 1932, **54**, 1429.

[2] B. Saxton and T. W. Langer, *ibid.*, 1933, **55**, 3638; T. Shedlovsky, A. S. Brown, and D. A. MacInnes, *Trans. Electrochem. Soc.*, 1934, **66**, 165.

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[8] J. F. C. Dippy and F. R. Williams, *ibid.*, 1934, 161.

[9] W. I. German, G. H. Jeffery and A. I. Vogel, *ibid.*, 1937, 1604.

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[12] G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, 1935, 1756.

[13] G. H. Jeffery and A. I. Vogel, *ibid.*, 1936, 1756.

[14] S. Basterfield and J. W. Tomecko, *Can. J. Research*, 1933, **8**, 447.

[15] W. L. German, G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, 1935, 1024.

See also vol. I, Tables 20, p. 214; 32, p. 338 and 33, p. 346.

TABLE III, 58

$$\varkappa = A\ e^{-E/RT}$$

Melt		A in mho.cm.$^{-1}$	E in k.cal.
Melt	%MO or M$_2$O$_3$		
CaO-SiO$_2$	20	148	26
	30	153	26
	35	164	24
	40	321	26
	45	1550	31
	50	247	23
	55	115	19
MnO-SiO$_2$	40	207	22
	50	180	18·6
	55	71	14·3
	60	176	15·7
	02.5	81	13
	05	870	21
	67·5	480	17·5
	70	160	11·5
	80	100	8
Al$_2$O$_3$-SiO$_2$	3	0·5	27
	5·5	1·2	26
	8	0·4	19
	10	0·5	22
	12	0·1	14

Accuracy: ±5%, but somewhat less near the m.p. where small changes in temperature cause relatively large changes in $\varkappa$.

TABLE III, 59

THERMODYNAMIC DISSOCIATION CONSTANTS OF BASES IN AQUEOUS AND ALCOHOLIC SOLUTION

Substance	pK	t °C.	Ref.	Substance	pK	t °C.	Ref.
Methylamine	10·64	25	(³)	o-Anisidine	4·49	25	(³)
Ethylamine	10·67	25	(³)	m-Anisidine	4·20	25	(³)
Propylamine	10·58	25	(³)	p-Anisidine	5·20	25	(³)
n-Butylamine	10·61	25	(³)	N-Ethylaniline	5·11*	25	(²)
iso-Propylamine	10·63	25	(³)	N-Methylaniline	4·85*	25	(³)
iso-Butylamine	10·42	25	(¹)	Pyrrolidine	2·00	25	(⁶)
iso-Amylamine	10·60	25	(¹)	N-Methylpyrrolidine	3·83	25	(⁶)
Dimethylamine	10·70	25	(¹)	Quinoline	5·00	25	(⁷)
Trimethylamine	10·81	25	(¹)	Quinine pK_1	5·70	20	(⁸)
Diethylamine	11·00	25	(¹)	pK_2	9·87	20	(⁸)
Triethylamine	10·72	25	(¹)	Atebrin pK_1	8·88	20	(⁸)
α ω-Diaminopentane	10·78	25	(¹)	pK_2	6·47	20	(⁸)
Ethanolamine	9·44	25	(²)	Acridine	4·11	20	(⁹)
Diethanolamine	8·88	25	(²)	Crystal violet	9·36	25	(¹⁰)
Triethanolamine	7·77	25	(²)	Pyrrole	0·4	20	(¹¹)
Cyclohexylamine	10·64	25	(²)	Diphenylamine	0·85	20	(¹¹)
Piperidine	11·12	25	(²)	Pyridine	5·19	25	(³)
1:2 Dimethylpiperidine	10·26	25	(²)	2-Amino-pyridine	7·14	25	(³)
1-Ethylpiperidine	10·41	25	(²)	Aniline	4·58	25	(²)
1-Propylpiperidine	10·23	25	(²)	o-Toluidine	4·39	25	(²)
1-N-Butylpiperidine	10·48	25	(²)	m-Toluidine	4·69	25	(³)
1 : 2 Dimethyl-tetra-				p-Toluidine	5·07	25	(³)
hydro-pyridine	11·42	25	(²)	N-Dimethylaniline	5·14	25	(³)
N-Methyl-m-toluidine	4·94	25	(²)	N-Methyl-o-toluidine	4·59	25	(²)
N-Methyl-p-toluidine	5·33	25	(²)				
N-Dimethyl-o-toluidine	5·86	25	(²)				
p-Chloraniline	4·07	25	(⁵)				
α-Naphthylamine	3·92	25	(²)	* In alcoholic solution			
β-Naphthylamine	4·11	25	(²)				

¹ C. W. HOERR, M. R. McCORKLE and A. W. RALSTON, J. Am. Chem. Soc., 1943, 65, 328.
² N. F. HALL and M. R. SPRINKLE, ibid., 1932, 54, 3469.
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⁴ R. BEALE and A. LIBERMANN, J. Chem. Soc., in Press 1951.
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¹⁰ R. J. GOLDACRE and J. N. PHILLIPS, J. Chem. Soc., 1949, 1724.
¹¹ N. F. HALL, J. Am. Chem. Soc., 1930, 52, 5123.
For dissociation constants of acids see Table 20, vol. I, p. 214 and Table III, 57.

TABLE III, 60

TRUE DEGREES OF DISSOCIATION OF ACIDS

(RAMAN spectra)

Nitric Acid at 25 °C.					
$c(N)$ †	4·51	6·60	8·00	10·80	11·89	14·28
a	0·828	0·678	0·49	0·39	0·82	0·14
$c(N)$	0·1	1	2	8	4	
a	0·997	0·978	0·95	0·90	0·85	

T. F. YOUNG and L. A. BLATZ, *Chem. Rev.*, 1949, **44**, 97.   Accuracy: ±2·5
† Concentration expressed as normality.

Values of a for Nitric Acid at higher temperatures			
$c(N)$	10·5	12·58	14·50
20° C.	0·352	0·212	0·114
60°	0·300	0·135	0·095
90°	0·226	0·105	0·022

O. REDLICH and J. BIGELEISEN, *J. Am. Chem. Soc.*, 1943, **65**, 1883.

Perchloric Acid at 20 °C.			
wt.%	c	$a c$	a
60	9·1	8·9	0·98
70	10·0	10·1	0·93
	12·0	10·3	0·86
84·8	14·7	6·1	0·45
	16·0	5·6	0·35

O. REDLICH *et al.*, *J. Am. Chem. Soc.*, 1944, **66**, 13.

Iodic Acid	
$c(N)$	a
0·4	0·56
0·8	0·40

N. R. RAO, *Ind. J. Phys.*, 1942, **16**, 71.

TABLE III, 60 (*Continued*)

Trichloracetic Acid	
$c(N) = 1.5$	$a = 0.60$

N. R. Rao, *Ind. J. Phys.*, 1943, 17, 832.

TRUE DEGREES OF DISSOCIATION (a) OF SALTS

(Conductance method)

		$c = 0.01$	0.02	0.05	0.1	0.5m
NaNO$_3$	([1])			0.991	0.985	
KNO$_3$	([1])	0.994	0.989	0.975	0.961	
AgNO$_3$	([1])	0.998	0.989	0.978	0.957	0.888
TlNO$_3$	([1])	0.984		0.946	0.917	
NaClO$_3$	([2])			0.992	0.986	
NaIO$_3$	([1])		0.996	0.988	0.984	
KIO$_3$	([1])	0.997	0.994	0.984	0.976	
KClO$_3$	([1])	0.994	0.989	0.977	0.968	
KBrO$_3$	([1])		0.993	0.984	0.977	
TlCl	([1])	0.972				
RbCl	([1])				0.990	
CsCl	([1])				0.981	

Accuracy not specified. As method involves one of successive approximation an evaluation of the accuracy is difficult.

TRUE DEGREES OF DISSOCIATION (a) OF SALTS (*Continued*)

(Conductance method)

CdCl$_2$ (18 °C.) ([2])				
c (mol/l.)	0.002	0.005	0.007	0.01
a	0.798	0.655	0.508	0.538

Ca(IO$_3$)$_2$ (25 °C.) ([3])				
$c . 10^4$ (mol/l.)	2.000	11.693	38.77	52.94	81.85
a	1	1	0.981	0.972	0.961

La[Fe(CN)$_6$] (25 °C.) ([5])				
c (mol/l.)	0.0016	0.0064	0.0144	0.0256	0.0400
a	0.63	0.50	0.49	0.52	0.57

Ca mandelate (25 °C.) ([4])				
$c . 10^4$ (mol/l.)	7.224	24.51	49.80	81.11	121.98
a	0.979	0.951	0.912	0.872	0.834

TABLE III, 60 (Continued)

TRUE DEGREES OF DISSOCIATION (α) OF SALTS

Ba succinate (25 °C.) ([1])				
$c \cdot 10^3$ mol/l.	1·764	2·081	4·778	
α	0·983	0·976	0·952	

Ba tartrate (25 °C.) ([2])				
$c \cdot 10^3$ mol/l.	1·451	2·474	4·622	
α	0·868	0·840	0·767	

Ba o-phthalate (25 °C.) ([3])				
$c \cdot 10^3$ mol/l.	1·608	2·002	4·081	
α	0·907	0·903	0·858	

Ca o-phthalate (25° C.) ([4])				
$c \cdot 10^3$ mol/l.	1·743	4·773	5·511	
α	0·871	0·876	0·818	

Ca tartrate (25 °C.) ([5])				
$c \cdot 10^4$ mol/l.	1·758	2·372	3·050	
α	0·805	0·725	0·714	

[1] C. W. DAVIES, *Trans. Faraday Soc.*, 1927, 23, 335.

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[6] C. W. DAVIES, *J. Chem. Soc.*, 1940, 87.

TABLE III, 61

SOLUBILITIES AND SOLUBILITY PRODUCTS OF SPARINGLY SOLUBLE SALTS IN WATER

Substance	Solubility (s) in g.mol/l. or Solubility product (sp) in terms of g.ions/l.		Temp.°C.	Ref
$Al(OH)_3$	0·96 $\cdot 10^{-5}$	s	29	([1])
$BaCO_3$	2·80 $\cdot 10^{-4}$	s	18	([2])
$BaCrO_4$	3·07 $\cdot 10^{-5}$	s	18	([3])
$BaSO_4$	0·957 $\cdot 10^{-5}$	s	25	([4])
CdS	1·14 $\cdot 10^{-28}$	sp	25	([5])
$CaCO_3$	13·4 $\cdot 10^{-5}$	s	25	([7])

TABLE III, 61 (*Continued*)

Substance	Solubility (s) in g.mol/l. or Solubility product (sp) in terms of g.ions/l.		Temp.°C.	Ref.
$Ca(COO)_2$	$1 \cdot 78 \ . \ 10^{-9}$	sp	25	[8]
$CaSO_4$	$2 \cdot 01 \ . \ 10^{-2}$	s	25	[9]
CoS	$3 \ . \ 10^{-26}$	sp	20	[9]
$Cu(IO_3)_2$	$3 \cdot 60 \ . \ 10^{-3}$	s	25	[10]
CuS	$3 \cdot 48 \ . \ 10^{-38}$	sp	25	[8]
Cu_2S	$8 \cdot 5 \ . \ 10^{-45}$	sp	25	[5]
Cu_2Cl_2	$7 \cdot 64 \ . \ 10^{-2}$	s	25	[11]
Cu_2I_2	$5 \cdot 0 \ . \ 10^{-12}$	sp	18	[5]
$Fe(OH)_2$	$1 \cdot 412 . \ 10^{-6}$	s	18	[12]
$Fe(OH)_3$	$3 \cdot 14 \ . \ 10^{-6}$	s	18	[13]
$Fe(COO)_2$	$3 \cdot 90 \ . \ 10^{-4}$	s	18	[14]
FeS	$5 \cdot 01 \ . \ 10^{-5}$	s	18	[15]
$PbCO_3$	$5 \cdot 25 \ . \ 10^{-6}$	s	20	[16]
$PbCrO_4$	$5 \cdot 27 \ . \ 10^{-7}$	s	20	[17]
PbI_2	$1 \cdot 64 \ . \ 10^{-3}$	s	20	[18]
PbS	$3 \cdot 62 \ . \ 10^{-11}$	s	25	[5]
$PbSO_4$	$1 \cdot 40 \ . \ 10^{-4}$	s	25	[19]
$Mg(NH_4)_2(SO_4)_2$	$2 \cdot 5 \ . \ 10^{-13}$	sp	25	[20]
$Mg(OH)_2$	$4 \cdot 6 \ . \ 10^{-24}$	sp	25	[21]
$MgCO_3$	$7 \cdot 46 \ . \ 10^{-4}$	s	100	[22, 23]
Hg_2Cl_2	$5 \cdot 42 \ . \ 10^{-19}$	sp	19·2	[24]
Hg_2Br_2	$3 \cdot 88 \ . \ 10^{-23}$	sp	19·2	[20]
Hg_2I_2	$10 \cdot 5 \ . \ 10^{-20}$	sp	19·2	[24]
Hg_2CrO_4	$2 \cdot 0 \ . \ 10^{-9}$	sp	25	[24]
NiS	$4 \ . \ 10^{-10}$	s	20	[9]
$AgCl$	$1 \cdot 60 – 1 \cdot 65 . \ 10^{-5}$	s	20	[25]
$AgBr$	$1 \cdot 86 \ . \ 10^{-6}$	s	20	[26]
AgI	$1 \cdot 0 \ . \ 10^{-16}$	sp	25	[5]
$AgCrO_4$	$1 \cdot 03 \ . \ 10^{-2}$	s	27	[27]
Ag_2S	$3 \cdot 28 \ . \ 10^{-25}$	sp	25	[5]
$AgSCN$	$1 \cdot 03 \ . \ 10^{-4}$	s	18	[28]
$AgCN$	$2 \cdot 10 \ . \ 10^{-7}$	s	18	[28]
$SrCO_3$	$1 \cdot 4 \ . \ 10^{-4}$	s	18	[2]
$Sr(COO)_2$	$2 \cdot 8 \ . \ 10^{-4}$	s	18	[2]
$SrSO_4$	$7 \cdot 5 \ . \ 10^{-4}$	s	18	[2]
ZnS	$1 \cdot 4 \ . \ 10^{-9}$	s	25	[9]
TlI	$6 \cdot 47 \ . \ 10^{-8}$	sp	25	[29]

TABLE III, 61 (*Continued*)

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TABLE III, 62

BUFFER SOLUTIONS OF KNOWN pH

Phthalate-HCl mixtures 20 °C.		
50 ml. of $M/5$ KHPhthalate	ml. of $M/5$ HCl to be added	Dilute to
2·2 pH	46·60 ml.	200 ml.
2·4	39·60	200
2·6	33·00	200
2·8	26·50	200
3·0	20·40	200
3·2	14·80	200
3·4	9·95	200
3·6	6·00	200
3·8	2·65	200

TABLE III, 62 (*Continued*)

Phthalate-NaOH mixtures 20 °C.

50 ml. of $M/5$ KHPhthalate	ml. of $M/5$ NaOH to be added	Dilute to
4·0 pH	0·40 ml.	200 ml.
4·2	3·65	200
4·4	7·35	200
4·6	12·00	200
4·8	17·50	200
5·0	23·65	200
5·2	29·75	200
5·4	35·25	200
5·6	39·70	200
5·8	43·10	200
6·0	45·40	200
6·2	47·00	200

KH_2PO_4-NaOH mixtures 20 °C.

50 ml. of $M/5$ KH_2PO_4	ml. of $M/5$ NaOH to be added	Dilute to
5·8 pH	3·66 ml.	200 ml.
6·0	5·64	200
6·2	8·55	200
6·4	12·60	200
6·6	17·74	200
6·8	23·60	200
7·0	29·54	200
7·2	34·90	200
7·4	39·34	200
7·6	42·74	200
7·8	45·17	200
8·0	46·85	200

Boric Acid, KCl-NaOH mixtures 20 °C.

50 ml. of $M/5$ H_3BO_3, $M/5$ KCl	ml. of $M/5$ NaOH to be added	Dilute to
7·8 pH	2·65 ml.	200 ml.
8·0	4·00	200
8·2	5·90	200
8·4	8·55	200
8·6	12·00	200
8·8	16·40	200

TABLE III, 62 (*Continued*)

50 ml. of $M/5$ H$_3$BO$_3$, $M/5$ KCl	ml. of $M/5$ NaOH to be added	Dilute to
9·0 pH	21·40 ml.	200 ml.
9·2	26·70	200
9·4	32·00	200
9·6	36·85	200
9·8	40·80	200
10·0	43·90	200

HCl-KCl mixtures of constant ionic strength $I_{(m)} = 0.1$.
Calculated on assumption that $f_{H_3O^+} = 0.84$

KCl molar	HCl molar	pH	Stock * KCl soln. ml.	Stock HCl soln. ml.	Dilute to	pH
0·00	0·10	1·076	0·00 +	59·5	100 ml.	(1·0) ($I_{(m)} = 0.119$) †
0·01	0·09	1·122	2·72 +	47·28	100	1·1
0·02	0·08	1·173	12·45 +	37·55	100	1·2
0·03	0·07	1·231	20·16 +	29·84	100	1·3
0·04	0·06	1·298	26·30 +	23·70	100	1·4
0·05	0·05	1·377	31·18 +	18·82	100	1·5
0·06	0·04	1·474	35·03 +	14·95	100	1·6
0·07	0·03	1·599	38·12 +	11·88	100	1·7
0·08	0·02	1·774	40·57 +	9·43	100	1·8
0·09	0·01	2·076	42·51 +	7·49	100	1·9
0·095	0·005	2·377	44·05 +	5·95	100	2·0
0·098	0·002	2·775	45·27 +	4·73	100	2·1
0·099	0·001	3·076	46·24 +	3·76	100	2·2

* stock KCl: 0·2 molar.   † For the pure HCl solution, the ionic strength is
stock HCl: 0·2 molar.   adjusted from 0·1 to 0·110 to give unit pH.

Sørensen's Phosphate mixtures
11·876 g. Na$_2$HPO$_4$. 2H$_2$O per l.   9·078 g. KH$_2$PO$_4$ per l.
Temperature 18 °C.

Na$_2$HPO$_4$ solution	KH$_2$PO$_4$ solution	pH
0·25 ml.	9·75 ml.	5·288
0·5	9·5	5·589
1·0	9·0	5·906
2·0	8·0	6·239
3·0	7·0	6·468
4·0	6·0	6·643

TABLE III, 62 (Continued)

Secondary	Primary	pH
5·0 ml.	5·0 ml.	6·818
6·0	4·0	6·979
7·0	3·0	7·168
8·0	2·0	7·381
9·0	1·0	7·781
9·5	0·5	8·043

SØRENSEN's citrate - NaOH mixtures

Citrate 21·008 g. cryst. Citric acid + 200 cc. N NaOH per l.

NaOH: 0·1N.

Temperature			10°	20°	30°	40°	50°	60°	70°
10·0 Citrate			4·93	4·96	5·00	5·04	5·07	5·10	5·14
9·5ml. Citrate	+ 0·5ml.	NaOH	4·99	5·02	5·06	5·10	5·13	5·16	5·20
9·0	,, + 1·0	,,	5·08	5·11	5·15	5·19	5·22	5·25	5·29
8·0	,, + 2·0	,,	5·27	5·31	5·35	5·39	5·42	5·45	5·49
7·0	,, + 3·0	,,	5·53	5·57	5·60	5·64	5·67	5·71	5·75
6·0	,, + 4·0	,,	5·94	5·98	6·01	6·04	6·08	6·12	6·15
5·5	,, + 4·5	,,	6·30	6·34	6·37	6·41	6·44	6·47	6·51
5·25	,, + 4·75	,,	6·65	6·69	6·72	6·76	6·79	6·83	6·86

L. E. WALBUM, *Ergeb. Physiol.*, 1912, 12, 393 and *Biochem. Z.*, 1920, 107, 219.
L. E. WALBUM (1920) has determined the pH values for Sørensen mixtures at temp. of 10°, 18°, 28°, 37°, 46°, 62° and 70° C. and has interpolated data for intervening temperatures. He finds that the alteration of pH with temp. is for the most part negligible for the phosphate mixtures, the glycocoll-HCl mixtures and the citrate-HCl mixtures (see pp. 739, 742 - 3 and 741 respectively).

TABLE III, 62 (*Continued*)

SØRENSEN'S BORATE - HCl MIXTURES

Borate Solution: 12·404 g. H_3BO_3 + 100 ml. N NaOH per l.

HCl: 0·1N.

Temperature				10°	20°	30°	40°	50°	00°	70°
10·0 ml. Borate				9·30	9·23	9·15	9·08	9·00	8·93	8·86
9·5 ,,	,,	+ 0·5 ml. HCl		9·22	9·15	9·08	9·01	8·94	8·87	8·80
9·0 ,,	,,	+ 1·0 ,,	,,	9·14	9·07	9·01	8·94	8·87	8·80	8·74
8·5 ,,	,,	+ 1·5 ,,	,,	9·06	8·99	8·92	8·86	8·80	8·73	8·67
8·0 ,,	,,	+ 2·0 ,,	,,	8·96	8·89	8·83	8·77	8·71	8·65	8·59
7·5 ,,	,,	+ 2·5 ,,	,,	8·84	8·79	8·72	8·67	8·61	8·55	8·50
7·0 ,,	,,	+ 3·0 ,,	,,	8·72	8·67	8·61	8·56	8·50	8·45	8·40
6·5 ,,	,,	+ 3·5 ,,	,,	8·54	8·49	8·44	8·40	8·35	8·30	8·26
6·0 ,,	,,	+ 4·0 ,,	,,	8·32	8·27	8·23	8·19	8·15	8·11	8·08
5·75 ,,	,,	+ 4·25 ,,	,,	8·17	8·13	8·09	8·06	8·02	7·98	7·95
5·5 ,,	,,	+ 4·5 ,,	,,	7·96	7·93	7·89	7·86	7·82	7·79	7·76
5·25 ,,	,,	+ 4·75 ,,	,,	7·64	7·61	7·58	7·55	7·52	7·49	7·47

SØRENSEN'S CITRATE - HCl MIXTURES

Citrate: 21·008 g. cryst. citric acid + 200 cc. N NaOH per l.

HCl: 0·1N.

Temperature 18 °C.

Citrate	HCl	pH
0·0 ml.	10·0 ml.	1·038
1·0	9·0	1·178
2·0	8·0	1·418
3·0	7·0	1·925
3·33	6·67	2·274
4·0	6·0	2·972
4·5	5·5	3·364
4·75	5·25	3·529
5·0	5·0	3·692
5·5	4·5	3·948
6·0	4·0	4·158
7·0	3·0	4·447
8·0	2·0	4·652
9·0	1·0	4·830
9·5	0·5	4·887
10·0	0·0	4·958

L. E. WALBUM, *Biochem. Zeit.*, 1920, 107, 219.

Volume Parts		pH at indicated					
Glycocoll	NaOH	10°	12°	14°	16°	18°	20°
9·5	0·5	8·75	8·70	8·66	8·62	8·58	8·54
9·0	1·0	9·10	9·06	9·02	8·97	8·93	8·8[
8·0	2·0	9·54	9·50	9·45	9·40	9·36	9·3:
7·0	3·0	9·90	9·85	9·80	9·75	9·71	9·6(
6·0	4·0	10·34	10·29	10·24	10·18	10·14	10·0(
5·5	4·5	10·68	10·63	10·58	10·53	10·48	10·4:
5·1	4·9	11·29	11·24	11·18	11·12	11·07	11·0:
5·0	5·0	11·53	11·48	11·42	11·36	11·31	11·2,
4·9	5·1	11·80	11·74	11·68	11·62	11·57	11·5:
4·5	5·5	12·34	12·28	12·22	12·16	12·10	12·0·
4·0	6·0	12·65	12·59	12·52	12·46	12·40	12·3:
3·0	7·0	12·92	12·86	12·80	12·73	12·67	12·6(
2·0	8·0	13·12	13·06	12·99	12·92	12·86	12·7:
1·0	9·0	13·23	13·16	13·09	13·03	12·97	12·9(
		42°	44°	46°	48°	50°	52°
9·5	0·5	8·07	8·03	7·99	7·95	7·91	7·8
9·0	1·0	8·41	8·37	8·32	8·28	8·24	8·1
8·0	2·0	8·81	8·76	8·72	8·67	8·63	8·5
7·0	3·0	9·13	9·08	9·03	8·99	8·94	8·8
6·0	4·0	9·53	9·48	9·43	9·38	9·33	9·2
5·5	4·5	9·86	9·81	9·76	9·71	9·66	9·6
5·1	4·9	10·40	10·35	10·29	10·24	10·18	10·1
5·0	5·0	10·64	10·59	10·54	10·48	10·43	10·3
4·9	5·1	10·87	10·81	10·75	10·69	10·64	10·5
4·5	5·5	11·38	11·32	11·26	11·20	11·14	11·0
4·0	6·0	11·65	11·59	11·53	11·47	11·41	11·3
3·0	7·0	11·91	11·85	11·79	11·73	11·66	11·6
2·0	8·0	12·08	12·02	11·96	11·89	11·83	11·7
1·0	9·0	12·19	12·13	12·06	12·00	11·94	11·8

62 (*Continued*)

NaCl–NaOH mixtures

7·505 g. Glycocoll + 5·85 g. NaCl per l.

temperature

22°	24°	26°	28°	30°	32°	34°	36°	40°
8·49	8·45	8·40	8·37	8·32	8·28	8·24	8·18	8·12
8·84	8·79	8·75	8·71	8·67	8·62	8·58	8·52	8·45
9·26	9·22	9·17	9·13	9·08	9·04	9·00	8·92	8·85
9·61	9·56	9·51	9·46	9·42	9·37	9·32	9·25	9·18
10·08	9·98	9·93	9·88	9·83	9·78	9·73	9·66	9·58
10·37	10·32	10·27	10·22	10·17	10·12	10·07	9·99	9·91
10·96	10·90	10·85	10·79	10·74	10·68	10·62	10·54	10·46
11·20	11·14	11·09	11·03	10·97	10·92	10·86	10·78	10·70
11·45	11·39	11·33	11·27	11·22	11·16	11·10	11·02	10·93
11·98	11·92	11·86	11·80	11·74	11·68	11·62	11·53	11·44
12·27	12·21	12·15	12·09	12·03	11·96	11·90	11·81	11·72
12·54	12·48	12·42	12·35	12·29	12·23	12·17	12·07	11·98
12·73	12·66	12·60	12·53	12·47	12·41	12·34	12·25	12·15
12·83	12·77	12·70	12·64	12·57	12·51	12·45	12·35	12·25

54°	56°	58°	60°	62°	64°	66°	68°	70°
7·82	7·78	7·74	7·69	7·65	7·61	7·56	7·52	7·48
8·14	8·10	8·06	8·02	7·97	7·93	7·88	7·84	7·79
8·53	8·49	8·44	8·40	8·35	8·30	8·26	8·21	8·16
8·84	8·79	8·74	8·70	8·65	8·60	8·55	8·50	8·45
9·23	9·18	9·13	9·08	9·03	8·98	8·93	8·88	8·82
9·56	9·51	9·46	9·41	9·35	9·30	9·25	9·20	9·15
10·07	10·02	9·96	9·90	9·85	9·79	9·74	9·68	9·62
10·32	10·26	10·20	10·14	10·09	10·04	9·98	9·93	9·87
10·52	10·46	10·40	10·35	10·29	10·23	10·17	10·11	10·05
11·02	10·96	10·90	10·84	10·78	10·72	10·66	10·60	10·54
11·28	11·22	11·16	11·10	11·03	10·97	10·91	10·84	10·78
11·54	11·47	11·41	11·35	11·28	11·22	11·16	11·09	11·03
11·70	11·64	11·57	11·51	11·44	11·38	11·31	11·25	11·18
11·80	11·74	11·67	11·61	11·54	11·48	11·41	11·35	11·28

TABLE III, 62 (*Continued*)

$M/15$ PHOSPHATE MIXTURES AT 20° AND 38 °C.
0·1N HCl of pH 1·08 used as standard of reference.

$M/15$ Na$_2$HPO$_4$	$M/15$ KH$_2$PO$_4$	pH det. at 20°	pH det. at 38°
49·6 ml.	50·4 ml.	6·809	6·781
52·5	47·5	6·862	6·829
55·4	44·6	6·909	6·885
58·2	41·8	6·958	6·924
61·1	38·9	7·005	6·979
63·9	36·1	7·057	7·028
66·6	33·4	7·103	7·076
69·2	30·8	7·154	7·128
72·0	28·0	7·212	7·181
74·4	25·6	7·261	7·230
76·8	23·2	7·313	7·288
78·9	21·1	7·364	7·338
80·8	19·2	7·412	7·384
82·5	17·5	7·462	7·439
84·1	15·9	7·504	7·481
85·7	14·3	7·561	7·530
87·0	13·0	7·610	7·576
88·2	11·8	7·655	7·626
89·4	10·6	7·705	7·672
90·5	9·5	7·754	7·726
91·5	8·5	7·806	7·770
92·3	7·7	7·848	7·825
93·2	6·8	7·909	7·877
93·8	6·2	7·948	7·919
94·7	5·3	8·018	7·977

A. B. HASTINGS and J. SENDROY, *J. Biol. Chem.*, 1924, **61**, 695.

4. Data on Electrode Processes and Electrode Potentials

TABLE IV, 1

STANDARD ELECTRODE POTENTIALS *

Irreproducibility of Measurements. The large effect of the state of the electrode surface, often stressed as a factor governing the potential associated with an irreversible electrode process, is generally contrasted with the small effect of this factor on reversible electrode potentials. A detailed examination of the literature does not support this contention. Effects of surface characteristics on reversible electrode potentials are probably partly due to the different degrees of mechanical strain in the metal induced by different modes of preparation. Impurities, particularly occluded gases, present in varying quantities, may have a considerable effect on the electrode potential by introducing other reactions at the electrode-solution interface. Lack of complete reversibility of the electrode reaction may also cause irreproducible measurements.

* See also vol. I, Tables 22, p. 251 and 25, p. 263.

TABLE IV, 1 (Continued)

Electrode Reaction	ε_0 (Volts)			Notes	References
	±1 mv. A	±1 cv. B	±? v. C		
$\tfrac{1}{2}N_2 + e_0^- \rightleftharpoons N_2'$	—	—	—3·2	Calc. Exptl. values irreproducible; electrode reaction irreversible (15, 90)	18, 89
$Li' + e_0^- \rightleftharpoons Li$	—	—3·01	—	Exptl. and calc. values somewhat discrepant. Mean value given; see also 33	2, 3
$Rb' + e_0^- \rightleftharpoons Rb$	—	—2·98	—	Fair agreement of independant determinations; but see 33	2, 5 (calc.); 3 (exptl.)
$Cs' + e_0^- \rightleftharpoons Cs$	—	—2·92	—	Calc. and exptl. values agree; but see also 2, 33	34 (calc.) 35 (exptl.)
$K' + e_0^- \rightleftharpoons K$	—	—2·92	—	Good concordance of results; but see 33	2, 5 (calc.) 3, 36 (exptl.)
$Ba'' + 2e_0^- \rightleftharpoons Ba$	—	—2·92	—	Calc. value; exptl. value —2·15 from fused salts measurement (33)	2, 37, 38
$Sr'' + 2e_0^- \rightleftharpoons Sr$	—	—2·89	—	Calc. value; exptl. value —2·86 (38), but see 33	2, 37, 88
$Ca'' + 2e_0^- \rightleftharpoons Ca$	—	—2·84	—	Calc. value; exptl. values —1·90 (38) to —2·76 (39)	2, 87
$Na' + e_0^- \rightleftharpoons Na$	—2·718	—	—	—	2, 3, 4, 5, 6
$La''' + 3e_0^- \rightleftharpoons La$	—	—	—2·4	Calc. and exptl. values very discrepant; see also (91)	2
$Mg'' + 2e_0^- \rightleftharpoons Mg$	—	—2·38	—	See 2, 34, 38, 41 for other calc. values; see also 42 and 43 for discrepant exptl. values	40

TABLE IV, 1 (Continued)

Electrode Reaction	e_0 (Volts)			Notes	References
	±1 mv. A	±1 cv. B	±? v. C		
$Th^{····} + 4e_0^- \rightleftharpoons Th$	—	—	-2.1	Calc. value	2
$Ti^{··} + 2e_0^- \rightleftharpoons Ti$	—	—	-1.75	Calc. value	2
$HfO^{··} + 2H^· + 4e_0^- \rightleftharpoons Hf + H_2O$	—	—	-1.7	Calc. value	2
$Be^{··} + 2e_0^- \rightleftharpoons Be$	—	-1.70	—	Calc. value; exptl. values, -1.1 to -1.9 (84, 85)	2, 88
$Al^{···} + 3e_0^- \rightleftharpoons Al$	—	-1.66	—	Mean of two calc. values; exptl. values very doubtful, see 45 and 46	84, 44
$ZrO^{··} + 2H^· + 4e_0^- \rightleftharpoons Zr + H_2O$	—	—	-1.5	Calc. values	2
$V^{··} + 2e_0^- \rightleftharpoons V$	—	—	-1.5	Calc. values (± 0.8)	2
$WO_4'' + 4H_2O + 6e_0^- \rightleftharpoons 8OH' + W$	—	—	-1.1	Calc. from est. value of entropy of WO_4''	2
$Mn^{··} + 2e_0^- \rightleftharpoons Mn$	—	—	-1.05	Calc. values	2, 92, 93
$Te + 2e_0^- \rightleftharpoons Te''$	—	—	-0.92	Calc. value; second dissociation const. of H_2Te not available; exptl. value, -0.84 (94)	18, 75
$UO_2^{··} + 4H^· + 6e_0^- \rightleftharpoons U + 2H_2O$	—	—	-0.82	Calc. entropy of ion uncertain.	2
$Se + 2e_0^- \rightleftharpoons Se''$	—	-0.78	—	Calc. values (independant data)	18, 47
$Zn^{··} + 2e_0^- \rightleftharpoons Zn$	-0.763	—	—	—	7, 8, 9, 10, 11
$H_3BO_3 + 8H^· + 8e_0^- \rightleftharpoons 3H_2O + B$	—	—	-0.73	Calc. value	2
$Cr^{···} + 3e_0^- \rightleftharpoons Cr$	—	—	-0.71	Calc. value	2
$SbO_2' + 2H_2O + 3e_0^- \rightleftharpoons Sb + 4OH'$	—	-0.67	—	Calc. and exptl. values	76, 77

TABLE IV, 1 (Continued)

Electrode Reaction	e_0 (Volts)			Notes	References
	±1 mv. A	±1 cv. B	±? v. C		
Ga''' + 3e_0 ⇌ Ga	—	−0.52	—	Exptl. value	48
S + 2e_0 ⇌ S''	—	−0.51	—	Calc. values based on thermal data for H_2S; agree with Ag | Ag_2S | H_2S electrode measurements; see also 51, 52	49, 50
Fe'' + 2e_0 ⇌ Fe	−0·402	−0.44	—	Exptl. values	18, 53, 54, 55
Cd'' + 2e_0 ⇌ Cd	—	—	—	—	5, 11, 12
In''' + 3e_0 ⇌ In	−0·385	−0·34	—	Exptl. values	56, 57
Tl' + e_0 ⇌ Tl	—	—	—	—	18, 14, 15
Co'' + 2e_0 ⇌ Co	—	−0·27	—	Exptl. values	58, 59, 60
Ni'' + 2e_0 ⇌ Ni	—	−0·23	—	See also 14, 63, for data in presence of H_2	61, 62
Mo''' + 3e_0 ⇌ Mo	−0·140	—	−0·2	Calc., mainly from estimated data	2
Sn'' + 2e_0 ⇌ Sn	—	—	—	—	18 (corrected by the value of e. for Pb given here),
Pb'' + 2e_0 ⇌ Pb	−0·126	—	—	Exptl. value	16, 17, 18, 19, 20, 21
D' + e_0 ⇌ $^1/_2 D_2$	—	−0·003	—	—	65
$HAsO_2$ + 3H' + 3e_0 ⇌ As + 2H_2O	—	0·25	—	Calc. from exptl. e.m.f. values of reaction As_2O_3 + 3H_2 ⇌ 2As + 3H_2O	2
BiO' + 2H' + 3e_0 ⇌ Bi + H_2O	—	0·32	—	Exptl. values	66, 67
Cu'' + 2e_0 ⇌ Cu	—	0·34	—	Exptl. values	68, 69, 70, 71, 72, 73

TABLE IV, 1 (Continued)

Electrode Reaction	e_0 (Volts)			Notes	References
	±1 mv. A	±1 cv. B	± ? v. C		
$\frac{1}{2}O_2 + H_2O + 2e_0^- \rightleftharpoons 2OH'$	0·401	—	—	Calc. values	78, 79, 80, 81, 82
$Cu' + e_0^- \rightleftharpoons Cu$	—	0·52	—	Calc. from equil., $Cu + Cu'' \rightleftharpoons 2Cu'$	116
$I_2 + 2e_0^- \rightleftharpoons 2I'$	0·530	—	—		18, 22, 28
$Te'''' + 4e_0^- \rightleftharpoons Te$	—	0·56	—	Calc. and exptl. values	74, 75
$Po'''' + 3e_0^- \rightleftharpoons Po$	—	—	0·56	Various exptl. data discrepant	95, 96
$Rh'' + 2e_0^- \rightleftharpoons Rh$	—	—	0·6	Calc. value; no knowledge of free energies of solution of oxides	2
$Hg_2'' + 2e_0^- \rightleftharpoons 2Hg$	0·798	—	—	—	18, 24
$Ag' + e_0^- \rightleftharpoons Ag$	0·799	—	—	—	18, 25, 26
$Pd'' + 2e_0^- \rightleftharpoons Pd$	—	—	0·88	Exptl. value; see also 97	99
$Ir''' + 3e_0^- \rightleftharpoons Ir$	—	—	1·0	Calc. value	2
$Br_2(l) + 2e_0^- \rightleftharpoons 2Br'$	1·066	—	—		27, 28
$Pt'' + 2e_0^- \rightleftharpoons Pt$	—	—	1·2	Calc. from data on $Pt(OH)_2 + 2H' + 2e_0^- \rightleftharpoons Pt + 2H_2O$	2
$Cl_2 + 2e_0^- \rightleftharpoons 2Cl'$	1·358	—	—	Calc. from e.m.f. data (100, 101)	18, 29, 80, 81, 82
$Au'''' + 8e_0^- \rightleftharpoons Au$	—	—	1·42	Calc. assuming the solubility of AuI to be analogous to that of CuI and AgI	2
$Au' + e_0^- \rightleftharpoons Au$	—	—	1·7	Calc.; calc. and exptl. values discrepant (81, 88)	2
$F_2 + 2e_0^- \rightleftharpoons 2F'$	—	2·85	—		86

TABLE IV, 1 (*Continued*)

Arrangement of Values of Standard Electrode Potentials. The agreement between the results of independent work is relatively poor, except for some of the softer metals where concordance of about 1 mv. is found among several independent determinations. For many elements, much larger discrepancies occur due partly to the difficulties of determination described above, but more frequently to lack of relevant data which makes for the accurate evaluation of e_0. On this account, the present collection distinguishes three classes of values.

In Table I, Column A refers to those elements for which there are apparently reliable independent data, concordant to within about 1 mv., which lead to an evaluation of the standard electrode potential.

Column B refers to those elements for which insufficiently reliable data are available for an accurate evaluation of the standard electrode potential. In this case, the most accurate results in the literature concerning the standard electrode potential are given with explanatory notes. The concordance between independent determinations is of the order of 1 cv.

Column C refers to those electrode potentials the values of which are of an extremely provisional nature.

Table IV, 2 refers to the standard potentials of some well-known half-cells, the values given being of an accuracy comparable with that of the values in column A.

TABLE IV, 2

STANDARD POTENTIALS OF SOME WELL-KNOWN HALF-CELLS *

Electrode	E_0 (volt)	References
$Pb(Hg) - PbSO_4 . SO_4''$	—0·351	114, 115
$Ag - AgI . I'$	—0·152	102
$Ag - AgBr . Br'$	0·071	98, 103, 104, 105, 106
$Hg - HgO . OH'$	0·098	107, 108
$Hg - Hg_2Br_2 . Br'$	0·140	109
$Ag - AgCl . Cl'$	0·222	98, 110, 111
$Hg - Hg_2Cl_2 . Cl'$	0·268	112, 113
$Hg - Hg_2SO_4 . SO_4''$	0·615	98
$Pb - PbO_2 . PbSO_4 . SO_4''$	1·685	115

* See also vol. I, Table 23, p. 258.

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Note: See also Table 22, Chap. VII.

TABLE IV, 3

STANDARD POTENTIAL OF THE Ag/AgCl ELECTRODE AS FUNCTION OF TEMPERATURE

Temp. °C.	E_0 mv.	Temp. °C.	E_0 mv.
0	0·23634	35	0·21563
5	·23392	40	·21200
10	·23126	45	·20821
15	·22847	50	·20437
20	·22551	55	·20035
25	·22239	60	·19620
30	·21912		

Accuracy: ± 0.05 mv.

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See also Table IV, 2.

TABLE IV, 4

LIQUID JUNCTION POTENTIALS

Solution	Composition in mol/l.			Total molality
	HCl	KCl	KNO$_3$	
A	—	4·185	—	4·185
B	—	3·103	1·035	4·138
C	0·043	3·061	1·035	4·139
D	0·043	4·147	—	4·190

1.   Liquid junction potentials calculated from HENDERSON equation.

Junction between the above solutions:	Potential at 25 °C. in mv.
A/B	—0·22
A/D	—0·48
B/C	—0·40
B/D	—0·28
C/D	—0·21
C/A	—0·70

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2.   K$_3$Fe(CN)$_6$/K$_4$Fe(CN)$_6$ junctions at 25 °C.

K$_3$Fe(CN)$_6$ conc. (mol/l.)	K$_4$Fe(CN)$_6$ conc. (mol/l.)	Mean conc. (mol/l.)	Liquid junction potential in mv.
0·5	0·05	0·275	31·5
0·4	0·04	0·22	31·0
0·2	0·02	0·11	28·5
0·1	0·01	0·055	25·9
0·1	0·005	0·0525	33·5
0·1	0·001	0·0505	52·2
0·02	0·001	0·0105	26·6
0·01	0·001	0·0055	18·1

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TABLE IV, 5

STANDARD OXIDATION-REDUCTION POTENTIALS AT 25 °C.

1. INORGANIC SYSTEMS

</div>

Reaction	e_0 volts	Ref.
$Cr^{\cdots} + e_0^- = Cr^{\cdot\cdot}$	$-0\cdot41$	1
$Ti^{\cdots} + e_0^- = Ti^{\cdot\cdot}$	$-0\cdot37 \pm 0\cdot01$	2
$Co(CN)_6''' + e_0^- = Co(CN)_6''''$	$-0\cdot83$	8
$V^{\cdots} + e_0^- = V^{\cdot\cdot}$	$-0\cdot20$	4
$TiO^{\cdot\cdot} + 2H^{\cdot} + e_0^- = Ti^{\cdots} + H_2O$	$0\cdot10$	5
$Sn^{\cdots\cdot} + 2e_0^- = Sn^{\cdot\cdot}$	$0\cdot154 \pm 0\cdot001$	6
$Cu^{\cdot\cdot} + e_0^- = Cu^{\cdot}$	$0\cdot167 \pm 0\cdot001$	7, 8
$VO^{\cdot\cdot} + 2H^{\cdot} + e_0^- = V^{\cdots} + H_2O$	$0\cdot314$	4
$PtCl_4'' + 2e_0^- = PtCl_4'' + 2Cl'$	$0\cdot72$	9
$Fe(CN)_6''' + e_0^- = Fe(CN)_6''''$	$0\cdot356$	10
$H_3AsO_4 + 2H^{\cdot} + 2e_0^- = H_3AsO_3 + H_2O$	$0\cdot550$	11, 8
$I_3' + 2e_0^- = 3I'$	$0\cdot535$	12, 8
$Fe^{\cdots} + e_0^- = Fe^{\cdot\cdot}$	$0\cdot771 \pm 0\cdot0005$	13, 29
$2Hg^{\cdot\cdot} + 2e_0^- = Hg_2^{\cdot\cdot}$	$0\cdot905 \pm 0\cdot001$	14
$HIO + H^{\cdot} + e_0^- = I' + H_2O$	$0\cdot99$	15
$V(OH)_4^{\cdot} + 2H^{\cdot} + e_0^- = VO^{\cdot\cdot} + 3H_2O$	$1\cdot000 \pm 0\cdot0005$	16, 17
$Tl^{\cdots} + 2e_0^- = Tl^{\cdot}$	$1\cdot25$	18
$PdCl_4'' + 2e_0^- = PdCl_4'' + 2Cl'$	$1\cdot288$	19
$Cr_2O_7'' + 14H^{\cdot} + 6e_0^- = 2Cr^{\cdots} + 7H_2O$	$1\cdot36$	20, 8
$HBrO + H^{\cdot} + 2e_0^- = Br' + H_2O$	$1\cdot33$	8
$MnO_2 + 4H^{\cdot} + 2e_0^- = Mn^{\cdot\cdot} + 2H_2O$	$1\cdot236 \pm 0\cdot002$	21
$ClO_4' + 8H^{\cdot} + 8e_0^- = Cl' + 4H_2O$	$1\cdot35$	8
$PbO_2 + 4H^{\cdot} + 2e_0^- = Pb^{\cdot\cdot} + 2H_2O$	$1\cdot456 \pm 0\cdot0005$	23, 24
$ClO_3' + 6H^{\cdot} + 6e_0^- = Cl' + 3H_2O$	$1\cdot45$	22, 8
$HClO + H^{\cdot} + 2e_0^- = Cl' + 3H_2O$	$1\cdot50$	8
$Mn^{\cdots} + e_0^- = Mn^{\cdot\cdot}$	$1\cdot51$	25
$Ce^{\cdots\cdot} + e_0^- = Ce^{\cdots}$	$1\cdot610 \pm 0\cdot001$	26
$H_2O_2 + 2H^{\cdot} + 2e_0^- = 2H_2O$	$1\cdot77$	8
$Co^{\cdots} + e_0^- = Co^{\cdot\cdot}$	$1\cdot842 + 0\cdot01$	27, 28

* $I_{(m)}$ = ionic strength.

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2. ORGANIC SYSTEMS

	Solvent	e_0 volts	
1,4-Naphthoquinone (N.Q.)	A	0·48	
2-Methyl 1, 4 N.Q.	B	0·40	
2-Phenyl 1, 4 N.Q.	B	0·45	Accuracy: ± 1 ev.
1,2-N.Q.	B	0·57	
4, Methyl 1, 2, N.Q.	B	0·53	

A   EtOH 50%, 0·1N HCl, 0·2N LiCl.

B   EtOH 70%, 0·2N HCl, 0·2N LiCl.

See L. F. Fieser and M. Fieser, *J. Am. Chem. Soc.*, 1935, **57**, 491.

TABLE IV, 5 (*Continued*)

Nitrosobenzene-phenylhydroxylamine system in 60% acetone-water 0·1N HCl.

	e_0 volts	
Nitrosobenzene	0·58	
2-Methyl-	0·59	
2,5-Dimethyl-	0·59	
2-Ethyl-	0·58	Accuracy: ± 1 cv.
2-Chloro-	0·59	
2-Bromo-	0·59	
3-Iodo-	0·58	

R. E. Lutz *et al.*, *J. Org. Chem.*, 1937, **2**, 68.

Anthraquinones	Solvent	e_0 volts	
2-Hydroxy-1, 4-anthraquinone	A	0·27	
1 : 4-Anthraquinone	A	0·40	Accuracy: ± 1 cv.

A = 50% aq. EtOH, 0·1N HCl, 0·2N LiCl.
L. F. Fieser, *J. Am. Chem. Soc.*, 1928, **50**, 405.

Quinones in alcoholic solution	e_0 volts	
Benzoquinone	0·71	
Toluquinone	0·66	Accuracy: ± 1 cv.
p-Xyloquinone	0·60	

H. R. Berliner, *J. Am. Chem. Soc.*, 1946, **68**, 49.

TABLE IV, 6

E.M.F.'S OF MOLTEN SALT DANIELL CELLS IN VOLTS

Pb	PbBr₂ (1) + PbCl₂	Br₂				

Mol fraction N_1		1·000	0·800	0·600	0·500	0·450
450°C	e.m.f.	1·0624	1·0736	1·0866	1·0959	1·1038
500°C	e.m.f.	1·0321	1·0447	1·0593	1·0687	1·0768
550°C	e.m.f.	1·0017	1·0156	1·0318	1·0415	1·0496

Ag	AgBr (1) + LiBr	Br₂				

Mol fraction N_1		1·0000	0·5937	0·4086	0·2548	0·1100
500°C	e.m.f.	0·7865	0·8085	0·8202	0·8301	0·8686
550°C	e.m.f.	0·7720	0·7901	0·8100	0·8216	0·8648
600°C	e.m.f.	0·7577	0·7836	0·7993	0·8128	0·8610

E.m.f. data accurate to $\pm 0·2$ mv.
E. J. Salström and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1930, **52**, 4048.

TABLE IV, 6 (Continued)

Zn │ ZnCl$_2$ │ Cl$_2$				
Temp. °C	501·0	527·8	541·0	565·2	575·5
e.m.f.	1·5721	1·5529	1·5440	1·5277	1·5199

E.m.f. data accurate to ±0·2 mv.

E. J. SALSTRÖM and J. H. HILDEBRAND, *J. Am. Chem. Soc.*, 1930, **52**, 4648.

Pb │ PbCl$_2$ │ Cl$_2$	e.m.f.	$1·2467 - 6·5 \;.\; 10^{-4} \,(t - 550)$
Cd │ CdCl$_2$ │ Cl$_2$	e.m.f.	$1·3421 - 6·29 . 10^{-4} \,(t - 599)$
Zn │ ZnCl$_2$ │ Cl$_2$	e.m.f.	$1·6050 - 4·6 \;.\; 10^{-4} \,(t - 427) - 8·03 . 10^{-7} \,(t - 427)$
Mg │ MgCl$_2$ │ Cl$_2$	e.m.f.	$2·5112 - 6·73 . 10^{-4} \,(t - 700)$

Accuracy: 0·2 mv. $t =$ temperature in °C.

R. LORENZ and H. VELDE, *Z. anorg. Chem.*, 1929, **183**, 81.

Ag │ AgCl │ Cl$_2$	Temp. 525 °C	e.m.f. 0·892
Pb │ PbCl$_2$ │ Cl$_2$	Temp. 525 °C	e.m.f. 1·255

Accuracy: ±1 mv.

S. A. PLATENEV and V. ROZOV, *Acta Physicochim. U.R.S.S.*, 1937, **7**, 841.

TABLE IV, 7

ABSOLUTE, NULL OR ZERO POINT POTENTIALS IN VOLTS, WITH REFERENCE TO THE
N-CALOMEL ELECTRODE

Electrode Metal*	Method	Ref.	Potential	Reproducibility
Hg	Electrocapillary curves	1	—0·50 v.	±0·01 v.
	Electrocapillary curves	2	—0·56 v.	±0·01 v.
	Deflection of Hg drops	3	—0·53 v.	
	Electrocapillary curves	5	—0·475 v.	±0·003 v.
Ga	Electrocapillary curves	4	—0·90 v.	±0·05 v.
Pt	Contact angle	12	0·0 v.	±0·1 v.

TABLE IV, 7 (Continued)

Electrode Metal	Method	Ref.	Potential	Reproducibility
Ag	Cataphoresis of suspended particles	6	—0·2 v.	
	Motion of massive metal	7	0·1 - 0·2 v.	
	Adsorption of ions	8	0·23 v.	
	Disturbance of potential by rubbing	9	0·19 v.	
	Electrode capacity in very pure solution and adsorption of ions in very pure solution	10	—0·24 v.	±0·02 v.
Ni	Salt effect on H overpotential (Validity of result depends on correctness of theoretical interpretation)	11	—0·54 v.	±0·02 v.

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TABLE IV, 8

HEAT OF ACTIVATION (ΔH^*) AND EXCHANGE CURRENT (i_0) FOR THE REACTION

$2H^+ + 2e \rightarrow H_2$ AT VARIOUS CATHODE MATERIALS

1. RELATIVELY RELIABLE VALUES

Electrode Material	Solution	a	i_0 amp./sq.cm.	ΔH^* k.cal./ g.mol.	Remarks	Ref.
Hg	0·20N H$_2$SO$_4$	0·52	$6 . 10^{-13}$	18·0	25 °C.	1
	0·25N H$_2$SO$_4$	0·50	$6·6 . 10^{-13}$	20·7	20°	2
	1·0N H$_2$SO$_4$	0·50	$4·9 . 10^{-13}$		20°	3
	1·0N H$_2$SO$_4$	0·40	$1·3 . 10^{-12}$		20°	
	0·2N D$_2$SO$_4$	0·52	$8 . 10^{-13}$	20·9	25°	4
	0·1N HCl	0·49	$1·7 . 10^{-12}$		22°	5

TABLE IV, 8 (*Continued*)

Electrode Material	Solution		a	i_0 amp./sq.cm.	ΔH^* k.cal./ g.mol.	Remarks	Ref.
Hg	0·1N	HCl	0·48	$9 . 10^{-12}$		20 °C.	3
	1·0N	HCl	0·49	$1·7 . 10^{-12}$	22·9 ±0·3	20°	6 *
	0·1N	HCl	0·50	$0 . 10^{-12}$	21·1 ±0·3	20°	7
	3N	HCl	0·48	$8·0 . 10^{-11}$	9·7 ±0·4	20°	6 *
	5N	HCl	0·45	$8·0 . 10^{-11}$	10·3 ±0·2	20°	6 *
	7N	HCl	0·54	$1·4 . 10^{-11}$	18·7 ±0·6	20° quoted energy of activation is at lower T's; it falls at higher T's.	6 *
	10N	HCl	0·61	$1·6 . 10^{-11}$	16·5 ±0·2	20°	6 *
	0·1N HCl in 36% methanolic solution		0·56	$5·1 . 10^{-12}$	23·6 ±0·5	20°	7
	0·1N HCl in 100% methanolic solution		0·56	10^{-11}	19·7 ±0·2	20°	7
	0·35N HCl in 100% methanolic solution		0·4 0·5	10^{-11}		—	8
	0·01 - 0·5N HCl in 100% ethanolic soln.		0·5	$2 . 10^{-11}$		—	9
Pb	1·0N HCl		0·48	$2 . 10^{-12}$		20° Surface scraped with knife; metal reduced by electrolytic evolution of H_2.	10

TABLE IV, 8 (*Continued*)

Electrode Material	Solution	a	i_0 amp./sq.cm.	ΔH^* k.cal./ g.mol	Remarks	Ref.
Ga	$0 \cdot 2N$ H_2SO_4	0·50	$1 \cdot 6 \cdot 10^{-7}$	15·2	87° liquid state	1
Woods Alloy	$0 \cdot 2N$ H_2SO_4	0·4	$1 \cdot 10^{-8}$	16·4	87°	1
Ni	$0 \cdot 001N$ HCl	0·63	$2 \cdot 10^{-7}$	6·7	20°	
	$0.01N$ HCl	0·64	$2 \cdot 10^{-7}$	9·9	Electrode an-	
	$0 \cdot 1N$ HCl	0·56	$9 \cdot 10^{-7}$	6·9	nealed H_2 c.800°	12
	$1 \cdot 0N$ HCl	0·53	$4 \cdot 10^{-6}$	16·3	in contact hysil glass	
	NH_4Cl in liq. NH_3	0·49	$7 \cdot 3 \cdot 10^{-9}$	7·0	−50°	18 *
Ag	$0 \cdot 001N$ HCl	0·47	$8 \cdot 10^{-7}$		20 °C. Electrode	
	$00 \cdot 1N$ HCl	0·45	$5 \cdot 10^{-7}$		annealed 700°C. in contact hysil glass.	
	$0 \cdot 1N$ HCl	0·65 0·48	$5 \cdot 10^{-7}$ $8 \cdot 10^{-6}$		lower c.d. range upper	
	$1 \cdot 0N$ HCl	0·97 0·45	$3 \cdot 10^{-6}$ $2 \cdot 10^{-4}$		lower upper	20
	$5 \cdot 0N$ HCl	0·83 0·48	$2 \cdot 10^{-7}$ $2 \cdot 10^{-5}$		lower upper	
Pt	$1 \cdot 0N$ HCl	0·41	$1 \cdot 6 \cdot 10^{-3}$	6–7	20° Extrapol. from values at c.d. 1 amp. per sq.cm. Over c.d. range 10^{-4} - 10^{-3} increases, markedly. Electrode smooth, acid etched, and heated to 600° in H_2 in contact with hysil glass.	14 19

TABLE IV, 8 (*Continued*)

2. VERY APPROXIMATE VALUES

Electrode Material	Solution	a	i_0 amp./sq.cm.	ΔH^* k.cal./ g.mol	Remarks	Ref.
Tl	1N HCl	0·7	10^{-11}		20° Surface scraped sharp knife	15
Bi	1N HCl	0·6	10^{-7}		18° Surface scraped sharp knife	16
Nb	1N HCl	0·6	10^{-11}		20°	15
Be	1N HCl	0·5	10^{-9}		20° Dissolved at c.d. 10^{-3} amp./sq.cm.	15
Cu		0·5	10^{-6}		20° Surface annealed in H_2 sealed to soda glass.	14
W	5N HCl	0·6	10^{-6}		20° Surface annealed in H_2, i_0 extrapol. from measmts. above 10^{-3} amp. sq.cm. Sealed to hysil glass	14
Pt	0·2N H_2SO_4	2·0	10^{-3}		Spongy Pt	17
Au	1N HCl	1·3	10^{-6}		18° Plated	16

(I) Note that knowing a and i_0, the overpotential η at any given c.d. can be calculated by means of the equation

$$\eta = 2.303 \frac{RT}{aF} \log \frac{i}{i_0}$$

provided that a is constant.

(II) Selection and division of the data in the above table is based upon a study of the relevant determinations. Particular importance was attached to the method of purifying the solution. Some of the values recorded in the similar table in (10) must be discarded as they indicate that the electrode surface was poisoned.

* Calculated from this reference, unpublished.

TABLE IV, 8 (*Continued*)

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See also J. A. V. BUTLER, *Electrical Phenomena at Interfaces in Chemistry, Physics and Biology*, Methuen, London, 1951; and Chapter XI, p. 423.

TABLE IV, 9

ELECTROKINETIC POTENTIALS ζ IN V. CALCULATED FROM THE STERN THEORY FOR AQUEOUS ELECTROLYTE SOLUTIONS AT THE Ag–H_2O INTERFACE AT 25 °C.

Electrode potential in volts	0·01N HCl	0·3N HCl	0·3N HCl / 0·2M BaCl$_2$	0·6N HCl	0·01 N HCl / 0·2M BaCl$_2$
			electrokinetic potentials in v.		
0	0·0	0·0	0·0	0·0	0·0
0·25	0·13	0·06	0·025	0·05	0·03
0·5	0·16	0·08	0·04	0·07	0·04
0·75	0·18	0·095	0·05	0·085	0·045
1·0	0·105	0·11	0·06	0·10	0·05
1·5				0·12	0·055

These figures show the dependence of ζ upon the "absolute" electrode potential measured with respect to the null-point potential. See Table IV, 7.

O. STERN, *Z. Elektrochem.*, 1924, 30, 508.
Calculated by B. E. CONWAY, *Thesis*, London, 1949.

TABLE IV, 9 *(Continued)*

ELECTROKINETIC POTENTIALS ζ AT THE GLASS-WATER INTERFACE

KCl conc. in μ mol/l.	ζ in mv.
10	73
25	72
50	70
100	67
250	62
500	58
1000	52
10^6	0

W. G. EVERSOLE and C. R. ESTEE, *J. Chem. Phys.*, 1943, 11, 63.

ELECTROKINETIC POTENTIALS ζ AT THE $BaSO_4$-WATER INTERFACE IN VARIOUS ELECTROLYTE SOLUTIONS

Electrolyte solution	ζ in mv.
Sat. aq. $BaSO_4$	26·6
$N/50,000$ K_2SO_4 + sat. aq. $BaSO_4$	24·3
$N/20,000$ K_2SO_4 + sat. aq. $BaSO_4$	19·8
$N/10,000$ K_2SO_4 + sat. aq. $BaSO_4$	14·7
$3N/10,000$ K_2SO_4 + sat. aq. $BaSO_4$	7·6
$6N/10,000$ K_2SO_4 + sat. aq. $BaSO_4$	3·6
$N/50,000$ $BaCl_2$ + sat. aq. $BaSO_4$	32·6
$N/20,000$ $BaCl_2$ + sat. aq. $BaSO_4$	39·8
$N/10,000$ $BaCl_2$ + sat. aq. $BaSO_4$	47·6
$6N/10,000$ $BaCl_2$ + sat. aq. $BaSO_4$	60·8
$N/1,000$ $BaCl_2$ + sat. aq. $BaSO_4$	60·6

A. S. BUCHANAN and E. HEYMAN, *Proc. Roy. Soc.*, 1948, A. 195, 150.

TABLE IV, 10

POLAROGRAPHIC HALF-WAVE POTENTIALS IN VOLTS WITH RESPECT TO NORMAL
CALOMEL ELECTRODE FOR REDUCTION OF VARIOUS CATIONS IN AQUEOUS SOLUTIONS

Cation reduced	Half-wave potentials in v.				
	In neutral or acid soln.	In $1N$ alkali	$1N$ NH_3 + $1N$ NH_4Cl	$1N$ KCN	10% tartrate or citrate
Ca¨	−2·23	−2·23	—	—	—
Li˙	−2·31	−2·31	—	—	—
Mg¨	−1·9	—	—	—	—
Sr¨	−2·13	−2·13	—	—	—
Na˙	−2·15	−2·15	—	—	—
K˙	−2·17	−2·17	—	—	—
Rb˙	−2·07	−2·07	—	—	—
Cs˙	−2·09	−2·09	—	—	—
NH₄˙	−2·07	−2·17	—	—	—
Ba¨	−1·94	−1·94	·— ·	—	—
Ra¨	−1·89	−1·89	—	—·	—
Al¨¨	−1·70	—	—	—	—
Mn¨	−1·55	·−1·74	−1·69	−1·37	−1·7
Cr¨	−1·42	−1·08	−1·74	—	—
Fe¨	−1·33	−1·56	−1·52	—	—
H˙	−1·60	—	—·	—	—
Co¨	−1·23	−1·44	−1·32	−1·2	—·
Ni¨	−1·09	—	−·1·14	−1·42	—
Zn¨	−1·06	·−1·41	−1·88	—	—
In¨¨	−0·63	−1·13	—	—	—
Cd¨	−0·63	−0·80	−0·85	−1·15	−0·87
Sn¨	−0·47	−1·18	—	—	−0·72
Pb¨	−0·46	−0·81	—	−0·74	−0·67
Tl˙	−0·50	−0·50	−0·52	—	−0·52
Sb¨¨	−0·21	−1·2	—	−1·17	—
Bi¨¨	−0·08	—	—	—	−0·41
Cu¨	−0·03	−0·52	—	—	−0·21
Cu˙	—	—	−0·54	—	−0·21
Au˙	—	−1·3	—	−1·5	—
Au¨¨	—	−0·6	—	—	—

Accuracy: ±0·05 - 0·10 v.

J. HEYROVSKY, *Polarographie*, Wien, Springer Verlag, 1941 p. 202-3.

TABLE IV, 10 (*Continued*)

ANODIC PROCESSES

Process (Conc. of anions, 0·001m)	Half wave potential. v.	Process	Half wave potential. v.
$2Hg + 2Cl' \rightarrow Hg_2Cl_2 + 2e$	+0·17	$Fe'' \rightarrow Fe''' + e$ (0·1N KHF$_2$)	+0·08
$Hg + CNS' \rightarrow HgCNS + e$	+0·10	$Fe'' \rightarrow Fe''' + e$ (NH$_3$, NH$_4$Cl)	—0·38
$2Hg + 2Br' \rightarrow Hg_2Br_2 + 2e$	+0·04	$Mn'' \rightarrow Mn''' + e$ (2N KOH	
$Hg + 2OH' \rightarrow HgO + H_2O + 2e$	+0·00	with tartrate)	—0·40
$2Hg + 2I' \rightarrow Hg_2I_2 + 2e$	—0·11	$Sn'' \rightarrow Sn'''' + 2e$ (HCl)	—0·06
$2Hg + 2CN' \rightarrow Hg(CN)_2 + 2e$	—0·42	$Sn'' \rightarrow Sn'''' + 2e$ (Tartrate or	
$Hg + S'' \rightarrow HgS + 2e$	—0·70	citrate buffer pH = 7)	—0·48
		$Sn'' \rightarrow Sn'''' + 2e$ (0·1N KOH)	—0·61
		$Ti''' \rightarrow Ti'''' + 2e$ (HCl)	—0·18

Process	Solution	Half wave potential. v.
$Cu' \rightleftharpoons Cu'' + e$	0·1N Na$_2$SO$_4$	—0·06
$Cu' \rightleftharpoons Cu'' + e$	1N NH$_3$, 1N NH$_4$Cl	—0·27
$Cu' \rightleftharpoons Cu'' + e$	Citrate buffer pH = 7	—0·21
$Cr'' \rightleftharpoons Cr''' + e$	CaCl$_2$ saturated	—0·55
$Fe'' \rightleftharpoons Fe''' + e$	1N Na oxalate	—0·80
$Fe'' \rightleftharpoons Fe''' + e$	Citrate buffer pH = 7	—0·40
$Fe'' \rightleftharpoons Fe''' + e$	1N KOH	—0·9
$Ti''' \rightleftharpoons Ti'''' + e$	CaCl$_2$ saturated	—0·15
$Ti''' \rightleftharpoons Ti'''' + e$	0·1N KCNS	—0·49
$Ti''' \rightleftharpoons Ti'''' + e$	Citrate or tartrate	—0·48
Hydroquinone $\rightleftharpoons$ quinone (Quinhydrone)	pH = 6·07	—0·011
$2H_2O \rightleftharpoons H_2O_2 + 2H' + 2e_0{}^-$	Neutral or alkaline	—1·1

Accuracy: ±0·05 - 0·10 v.

J. HEYROVSKY, *Polarographie*, Wien, Springer Verlag, 1941. p. 204.

TABLE IV, 11

ELECTROPHORETIC MOBILITIES

MOBILITIES IN cm.^{2}/sec./volt . 10^4 AT 0 °C.

pH	2	3	4	5	6	7	8	9
Pepsin [a]	—0·08	—0·23	—0·45					
Ovalbumin [1]			+0·19	—0·15	—0·47	—0·62		
Serum Albumin [a]			+0·40	—0·14	—0·48	—0·65	—0·75	
γ Globulin [a]				+0·25	+0·00	—0·12	—0·16	
Ribonuclease [a]						+0·18	—0·07	—0·39

The negative sign indicates that the ampholyte carries a net negative charge and migrates to the anode, whilst the positive sign indicates a cathophilic mobility. Accuracy: ±5%.

[1] Proteins of Egg White: L. G. LONGSWORTH, LARSON and D. A. MacINNES, *J. Am. Chem. Soc.*, 1940, **62**, 2587.

[a] H. A. ABRAMSON, L. S. MOYER and M. H. GORIN, *Electrophoresis of Proteins and the Chemistry of Cell Surfaces*, New York, Reinhold Publ. Corp., 1942, p. 81.

MOBILITIES OF GLYCINE, ALANINE AND GLYCYL-GLYCINE
IN cm.^{2}/sec./volt . 10^4 AT 0 °C.

pH	Glycine in HCOOH	Alanine in		Glycyl-glycine in HCOOH
		HCOOH	CH$_3$COOH	
2·3	10·85	8·6		12·6
2·4	9·3	7·7		12·2
2·6	7·3	6·1	5·5	11·25
2·7	6·35	5·3	4·7	10·7
2·9	4·6	3·85	3·85	9·3
3·0	3·9	3·2	2·8	8·6
3·2	2·65	2·2	1·9	6·95
3·6				3·9
3·8				2·8
3·9				2·3

TABLE IV, 11 (*Continued*)

MOBILITIES OF GLYCINE, ALANINE AND GLYCYL-GLYCINE
IN cm.^{2}/sec./volt . 10^4 AT 0 °C.

*p*H	Glycine in NH$_3$ aq.	Alanine in NH$_3$ aq.
9·3	—4·2	—2·6
9·4	—4·9	—3·1
9·6	—6·6	—4·4
9·8	—8·3	—5·9
9·9	—9·2	—6·7
10·1	—10·8	—8·35
10·2	—11·5	—9·1
10·4	—12·7	—10·5
10·5	—13·2	—11·1
10·7	—13·9	—12·1
10·8	—14·2	—12·5

H. SVENSSON, A. BENJAMINSSON and I. BRATTSTEN, *Acta Chem. Scand.*, 1949, 3, 307.

EXAMPLES

EXAMPLES*

The problems which follow are graded in order of difficulty. In general the first two are easy applications of the concepts developed in the corresponding chapter; the following six are of average difficulty; and the final two are adapted for the less elementary student.

Answers to all problems and notes on the solution of the more difficult type are given on p. 816. Since many are taken from the original literature further information can be gained by consulting the reference given. The student is not expected to arrive at exactly the numerical answers given since different methods of computation (particularly if graphical) may lead to small discrepancies in the result.

CHAPTER I

I-1.   The velocity of a boundary of HCl with LiCl is followed in aqueous solution. It moves 15·0 cm. in a tube 1 cm. diameter in 21 minutes when the current is 11·54 milliamp. If the concentration of the HCl is 0·01065N, what is the transport number of the hydroxonium ion?

I-2.   A conductance cell is filled with 0·01 normal KCl at 25 °C. and placed in a bridge network having equal ratio arms. The resistance required for balance is 2,440 ohms. Evaluate the cell constant.

The cell is now filled with a 0·02N solution of BaCl$_2$, and the resistance required is 1,442 ohms. What is the equivalent conductance of BaCl$_2$ at this concentration? (Specific conductance of KCl is given in Table I, Chapter I).

I-3. In an experiment to determine the absolute conductance of 0·1 N aqueous KCl, a right cylindrical cell of length 32·697 cm., and volume 53·362 ml. at 0 °C., with plane circular electrodes at the extremities was used. The resistance of the solution in the cell was measured at 0 °C. using a bridge network ABCD, where AB, BC, were the ratio arms 100 ohms and 1000 ohms respectively and CD was the conductance cell. For balance the value of AD was found to be 280·98 ohms. What is the specific conductance of 0·1 N aqueous KCl?

I-4. JONES and BRADSHAW (*J. Am. Chem. Soc.*, 1932, **54**, 138) determined the transport number of Li in LiCl using a cell with Ag/AgCl electrodes. After an electrolysis of four hours the weights of silver deposited in coulometers on either side of the cell, in series with it, were 0·51677 and 0·51682 g. The concentration of the middle compartment remained unchanged at 7·6176 mg.LiCl/g. H$_2$O while the concentration in the anode compartment (which contained 128·14 g. of solution) decreased to 7·1141 mg.LiCl/g.H$_2$O. What is the transport number of the chloride ion in this solution?

I-5. A potentiometer wire of total length 1 metre is used to compare the e.m.f. of a DANIELL cell with that of a WESTON cell at 20 °C. If the length of the wire required to balance the WESTON cell is 50·86 cm. and that for the DANIELL cell is 52·45 cm., what is the e.m.f. of the DANIELL cell? What will the balance point be if a 10 ohm resistance is placed (a) in series with the DANIELL cell (b) in parallel with the DANIELL cell (internal resistance of DANIELL cell is 0·72 ohms; e.m.f. of WESTON cell is 1·018 v.)?

I-6. A 0·1002N solution of AgNO$_3$ was electrolysed between pure silver electrodes for 6 hours. The cathode was found to have gained 0·1207 g. in weight and the 86·25 ml. of solution in the cathode compartment were titrated and found to be 0·0941N

with respect to silver nitrate. The anode compartment contained 106·51 ml. of 0·1051N silver nitrate. What is the transport number of the silver ion in this solution?

I-7.   A hydrogen coulometer and an iodine coulometer were connected in series. During a passage of current for 1 hour 95·0 ml. of hydrogen were collected at 19 °C., the atmospheric pressure being 74·4 cm of Hg. The iodine released was titrated with a 0·1N solution of As_2O_3 and 78·34 ml. were required to neutralise it. Assess the error of the hydrogen coulometer.

I-8.   The current passing through the circuit in Question 7 is also measured by passing it through a calibrated 10 ohm resistance (calibrated value 10·24 ohm) and the potential across this resistance measured by means of a slide wire potentiometer at 19 °C. using a WESTON standard cell in opposition to the p.d. being measured. 81·51 cm. of the wire are required to balance the resultant p.d. and 73·26 cm. to balance the standard cell alone. What is the current flowing and how does this agree with the value obtained from the iodine coulometer?

I-9.   In a certain electrode-solution system, bubbles of hydrogen gas are evolved and it is found that the pressure of hydrogen inside the bubble is equal to the pressure of hydrogen outside it. The radius of the bubble is r and its surface tension γ. What is its electrostatic potential?

I-10.   The space between two metal plates, of large area, d cm. apart, is filled with ionized gas at a uniform pressure (1 atmosphere). A gaseous ion is formed at the right hand plate at time $t = 0$. The charge density on the plates is σ and is constant with time. At a time t' an additional electric field F is impressed on the system. F varies coulombically from a position (at which the conditions are N.T.P.) h cm. below the ion. The dielectric constant of a gas may be taken as $\varepsilon = 1 + mp$, where p is the pressure in atmospheres and m is a constant.
   Find how long the ion takes to cross from one plate to the other (assume that the viscous resistance of the gas to the ion is negligible).

CHAPTER II

II-1. The molar heat capacity at constant pressure of alumina is given by $C_p = 22{\cdot}08 + 8{\cdot}971 \, . \, 10^{-8} \, T + 0{\cdot}5225 \, . \, 10^{6} \, T^{-2}$. What is the minimum amount of heat required to raise one mole of alumina from 25 °C. to 1500 °C.? What is the entropy change of the alumina during such a process?

II-2. SCHUMANN, ASTON and SAGENKAHN (*J. Am. Chem. Soc.*, 1942, **64**, 1089) give the following values for the molar heat capacity of isopentane.

T °K.	C_p	T °K.	C_p
20	8·25	120	29·68
25	4·82	150	80·72
80	6·00	186	81·95
50	10·41	240	35·20
70	15·00	260	36·59
110	20·75	290	40·49

Fusion takes place at 113·39 °K., the latent heat of fusion being 1226·3 cals/g.mol. Extrapolate the values of the heat capacity to 0 °K using the DEBYE equation and obtain a value of the standard entropy of isopentane by a graphical integration.

II-3. Show that the JOULE-THOMSON coefficient $\left(\dfrac{\partial T}{\partial P}\right)_{\mathrm{H}}$ for any gas may be represented by the equation

$$\left(\frac{\partial T}{\partial P}\right)_{\mathrm{H}} = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right].$$

Substitute values for V and $\left(\dfrac{\partial V}{\partial T}\right)_P$ for a gas obeying the VAN DER WAALS equation (assuming that $V = \dfrac{RT}{P}$ in the correction terms) and show that the JOULE-THOMSON inversion temperatures may be obtained from the equation

$$T_i^2 - \frac{2a}{Rb}\,T_i + \frac{3aP}{R^2} = 0\,.$$

Calculate values of these for ethane, for which $a = 5.46$ litre² atm.mol⁻² and $b = 6.47 . 10⁻²$ at 1 atm.litre.mole⁻¹.

II-4. Show that the entropy of 1 mole of a mixture of i ideal gases is greater than that of the separate gases under the same external pressure by

$$- R \sum_i N_i \ln N_i .$$

(N_i is the mole fraction of i in the mixture).

II-5. From the following data (M. DE K. THOMSON, *The Total and Free Energies of Formation of the Oxides of 32 Metals*, New York, 1942) evaluate expressions for the free heat content of the red and yellow monoxides of lead,

$$Pb_{(s)} \qquad C_P = 5.77 + 2.02 . 10^{-3} T ;$$
$$O_{2 (g)} \qquad C_P = 9.268 + 0.870 . 10^{-3} T - 42.82 T^{-1} ;$$
$$PbO_{(s, \text{ red or yellow})} \quad C_P = 10.33 + 3.18 . 10^{-3} T .$$

The standard heat of formation (ΔH_{298}) for the red oxide is —52,460 cal.mole⁻¹ while that for the yellow oxide —52,060 cal. mole⁻¹. The standard free heat content of formation (ΔG_{298}) for the red oxide is —45,238 cal.mole⁻¹, while that for the yellow oxide is —45,138 cal.mole⁻¹. Hence, derive an equation for the free heat content change in the transition from yellow to red oxide and calculate the transition temperature. Which oxide is stable at room temperature?

II-6. The energy of the bond O—H may be defined as half the heat content change occurring when a water molecule is formed from two hydrogen atoms and an oxygen atom, *i.e.* O + 2H → H₂O, $\Delta H = —220.4$ k.cal., and the O—H bond energy is —110.2 k.cal. (*cf.* L. PAULING, *Nature of the Chemical Bond*, Cornell Univ. Press 1944). Calculate the bond energies of C—H, C—C, and C=C bonds if the ΔH of formation of atomic hydrogen is +51.7 k.cal./g.atom; atomic oxygen is +59.2 k.cal./g.atom; H₂O(g) is —57.80 k.cal./ g.mol; CH₄ (g) is —17.89 k.cal./g.mol.; C₂H₆(g) is —20.24 k.cal./ g.mol., and C₂H₄(g) is +12.56 k.cal./g.mol. The heat content change when 1 g.atom of diamond is vapourised is +124.3 k.cal.

Hence calulate the total bond energy of benzene assuming a KEKULÉ structure. Also calculate this quantity if the heat of combustion of benzene, $\Delta H = -789\cdot2$ k.cal./g.mol, and the ΔH of formation of CO_2 is $-94\cdot05$ k.cal./g.mol. Suggest a reason for any discrepancy in these values for the total bond energy of benzene.

II-7.   Calculate the partial molar volume of potassium iodide in aqueous solutions of $0\cdot2$, 1, 8 and 5 molal, using the following data:

wt.% KI	Density	wt.% KI	Density
1	1·00434	24	1·20865
4	1·02677	80	1·26849
10	1·07446	40	1·39268
14	1·10860	50	1·54208
20	1·16383		

II-8.   If γ is the free heat content at an interface of unit area in excess of that which would exist if both phases were uniform up to a mathematical surface dividing them, and Γ_1, Γ_2 are the surface excesses of the two components in the system per unit area, show that $d\gamma = -S_s\, dT - \Gamma_1\, d\mu_1 - \Gamma_2\, d\mu_2$ (S_s is the surface excess of entropy per unit area).

If the mathematical surface is so placed that the surface excess of one component vanishes, show that the surface excess of the second is given by, $\Gamma_2 = -\dfrac{c_2}{RT}\dfrac{\partial\gamma}{\partial c_2}$ in a dilute solution.

II-9.   Show that $\dfrac{\left(\dfrac{\partial P}{\partial V}\right)_s}{\left(\dfrac{\partial P}{\partial V}\right)_T} = \dfrac{C_P}{C_v}$.

II-10.   Radiation of wavelength 7500 Å at an intensity of 10^4 candle power/cm^2 is directed onto a thermopile with junctions covering an area of 1 cm^2. One side of the thermopile is thus raised from 20 °C. to 20·1 °C. Calculate the maximum amount of electrical energy (in watts) which could become available for measurement on external instruments (1 c.p. $= 2 . 10^{14}$ quanta/sec.).

CHAPTER III

III-1. Extend Table 8 by calculating values of the lattice energy for the caesium halides. CsF crystallises in the rock salt structure and the remainder in the CsCl structure.

	r_0 (Å)	n
CsF	3·00	9·5
CsCl	3·58	10·5
CsBr	3·73	11·0
CsI	3·96	12·0

III-2. Check the results of Question 1 using the BORN-HABER cycle
$$L_{Cs} = 19\cdot1 \qquad I_{Cs} = 89\cdot4 \; .$$

	W	$\frac{1}{2} D_{Hal}$	E_{Hal}
CsF	—131·5	32·2	—98·5
CsCl	—106·6	28·9	—92·5
CsBr	— 97·5	26·9	—87·1
CsI	— 83·9	25·4	—79·2

All in k.cal.

III-3. Calculate the heats of solvation for CsF, CsCl, CsBr, CsI at 291 °K. if the initial heats of solution of these substances in water are respectively —8·37, +4·75, +6·73, and +8·25 k.cal./g.mol. The specific heats of the crystals may be taken as those of the corresponding rubidium salts (use values of U_0 from Question 1). Calculate these solvation heats theoretically and compare with the above experimental values.

(Radius of Cs^+ = 1·70 Å. ε_{H_2O} at 278 °K. = 86·10; at 288 °K. = 82·19; at 298 °K. = 78·48, and at 308 °K. = 74·94).

III-4. Evaluate the percentage error caused by using equation (4) instead of equation (3) for the interaction of a water molecule with a sodium ion at closest approach (diam. H_2O = 3·0 Å, diam. Na = 2 Å) assuming the distance between the poles of the water dipole to be 0·5 Å and the angle φ is 10°.

At what distance is the approximation within 1% of (8) when $\varphi = 0°$, $45°$, $60°$ and $90°$?

III-5. Show that the energy of interaction of a charge e_0 with a quadrupole composed of two linearly oriented dipoles in opposite senses each with charges $\pm e$ and length l is approximately given by

$$- \frac{2\,e\,e_0\,l^2 \cos^2 \varphi}{r^3},$$

where r is distance between the charge and the mid point of the quadrupole and φ is the angle of inclination of the quadrupole to the field. What is the relation between the distances at which the interaction energy between an ion and an HCl molecule will be equal to that between the same ion and a CO_2 molecule if $\varphi = 60°$ in both cases. ($\mu_{HCl} = 1·03$ debye; $\mu_{O-O} = 2·8$ debye; C—O distance is $1·22$ Å).

III-6. Show that the total energy of interaction between two mutually induced dipoles of moment μ_1, μ_2 and polarisability a_1, a_2 respectively is

$$-\frac{1}{2r^6}\left[a_2\,\mu_1^2\,(1 + 3\cos^2 \theta_1) + a_1\,\mu_2^2\,(1 + 3\cos^2 \theta_2)\right].$$

θ_1, θ_2, are the angles between the axis of the dipoles and the line length r joining the centres of the two axes.

If the dipoles are identical and are subject to random rotation, what is the energy of interaction?

III-7. Using the result of Question 6, show that an approximate measure of the energy due to dispersion forces between two atoms is given by

$$U = -\frac{4\,a^2\,I}{r^6},$$

where a is the polarisability and I the ionisation energy. For a gm.molecule LONDON (*Trans. Faraday Soc.*, 1987, 33, 8) has shown that $U = 3·68\left(\dfrac{N_A}{V}\right)^2 I\,a^2$ in k.cal. which is approximately equal to the heat of sublimation for rare gas crystals.

Calculate the heat of sublimation for neon.

($a = 0.89 \cdot 10^{-24}$ cc.; density $= 1.46$ g./cc.; $I = 495$ k.cal.).

III-8. Calculate the solvation number of the following ions whose standard entropies at 25 °C. are given, in cal.deg.$^{-1}$mole^{-1}.

H$^+$	0.00	Na$^+$	13	Rb$^+$	23
F$^-$	-6	Cl$^-$	14.7	I$^-$	26.5

The absolute entropy of the chlorine ion may be taken as 18.8 cal.deg^{-1}mole^{-1}. The molar heat of fusion of water at the melting point is 1438 cal. The molar heat capacity of water is 18 cal. and of ice, 9 cal.

III-9. PASSYNSKY (*Acta Physicochim. U.R.S.S.*, 1938, **8**, 835) evaluated the solvation number of salts from the compressibility of their aqueous solutions. The immediate solvent sheath of the ion was considered to be subjected to such a great pressure by the electrical forces that it was virtually incompressible by external forces. Thus the decrease of compressibility as the ionic concentration is increased corresponds to an increase in the amount of solvent removed by solvation. The adiabatic compressibility (β) was obtained from measurements of the velocity of sound (V),

$$\beta = \frac{1}{V^2 \rho},$$

where ρ is the density.

Show that the number of grams of water (h) attached to a gram of solute is given by,

$$h = \frac{\left(1 - \dfrac{V_0^2 \rho_0}{V^2 \rho}\right)\left(100 - g\right)}{g},$$

where V_0 and ρ_0 refer the to pure solvent, and g is the number of grams of solute dissolved in 100 grams of solution. Suggest probable values of the solvation numbers at infinite dilution for NaCl and NaI.

	g	V (m.sec.$^{-1}$)	ρ (g.cm.$^{-1}$)
NaCl	1.0	1497.0	1.005
	5.31	1547.0	1.040
	21.25	1741.0	1.157

	g	V	ϱ
NaI	1·32	1484·7	1·009
	8·19	1485·0	1·024
	13·78	1488·7	1·115

The velocity of sound in pure water is 1484·0 m./sec.

III-10. Evaluate the solvation number of lithium in 0·01, 0·02, 0·05 and 0·1M solution of LiCl using the DEBYE-HÜCKEL equation for the steady motion of an ion (see Chap. V) and compare the results with those obtained at infinite dilution.

c	l	n_+
Inf. dil.	115·03	0·3364
0·01M	107·3	0·3289
0·02	104·7	0·3261
0·05	100·1	0·3211
0·10	95·86	0·3168

The crystal radius of Li is 0·70 Å.

CHAPTER IV

IV-1. The freezing points of solutions containing 0·01 and 0·05 g.mol. of Na_2SO_4 per 1000 g. of water were found to be —0·0525 °C. and —0·210 °C. respectively. Calculate the apparent (classical) degree of dissociation if the latent heat of fusion of ice is 79·67 cal./g.

IV-2. The conductance of nitric acid in methanol and ethanol measured by MURRAY-RUST and HARTLEY (*Proc. Roy. Soc.*, *A*, 1929, **126**, 84) is given below. Investigate the applicability of OSTWALD's dilution law to these systems.

MeOH	$c . 10^4$	Λ	EtOH	$c . 10^4$	Λ
$\Lambda_\infty = 203$	0·9662	178·69	$\Lambda_\infty = 87·5$	1·0333	52·56
	1·8143	165·17		2·2022	42·44
	3·0753	151·00		3·8952	35·14
	4·7296	137·60		6·0849	29·91
	6·5835	124·16		8·5763	26·29
	9·1630	116·82		11·4924	23·43

IV-3. McCULLOUGH (*J. Am. Chem. Soc.*, 1942, **64**, 2672) investigated the absorption of light in solutions of diphenyl selenium bromide in carbon tetrachloride. This substance dissociates into diphenyl selenium and Br_2. The ratio I/I_0 was determined for various concentrations and wavelengths, the thickness of the cell being 1·30 cm.

$\lambda_{(m\mu)}$	I/I_0		
	$1·62 . 10^{-4}M$	$2·00 . 10^{-4}M$	$4·00 . 10^{-4}M$
340	0·500	0·386	
360	0·632	0·537	0·140
380	0·742	0·680	0·318
400		0·793	0·548

Evaluate the dissociation constant if the molar extinction coefficients are:

$\lambda_{(m\mu)}$	$\varepsilon_{\varphi_2 SeBr_2}$	$\varepsilon_{\varphi_2 Se}$	ε_{Br_2}
340	6910	3·5	5·4
360	4670	1·3	26
380	2620	0·6	87
400	1130	0·4	166

IV-4. PERMAN and URRY (*Proc. Roy. Soc.*, *A*, 1929, **126**, 44) give the following results for the osmotic pressure of aqueous KCl solutions at 50 °C.:

c (g./100 g.)	P (atmos.)	Density
2·0	9·73	1·001
5·0	27·01	1·019
10·0	61·30	1·05
15·0	109·18	1·08
22·50	196·8	1·13

Evaluate the osmotic coefficients.

IV-5. LARSEN and HUNT (*J. Phys. Chem.*, 1935, **39**, 877) measured the vapour pressure over solutions of NH_4NO_3 in liquid NH_3. Ammonia gas at these pressures obeys the equation

$$\frac{PV}{RT} = 1 - 1 \cdot 856 \cdot 10^{-4}\, P - 2 \cdot 578 \cdot 10^{-8}\, P^2 \, ;$$

P is in cm. of Hg. Calculate the activity of the solvent in these solutions.

$m_{NH_4NO_3}$	P (cm.)	$m_{NH_4NO_3}$	P (cm.)
22·8	235·8	1·40	733·4
15·2	373·8	1·14	736·6
11·2	489·1	0·917	739·2
6·38	643·8	0·683	742·0
4·19	692·0	0·508	744·0
2·94	718·6	0·411	745·1
1·97	762·5	0	750·6

IV-6.   JONES and HECKMAN (*J. Am. Chem. Soc.*, 1947, **69**, 536) calculated the activity of KIO_4 from measurements of the solubility of this substance in solutions of NaCl and $LiNO_3$ estimated iodometrically. The solubility of KIO_4 in pure water is 0·02248 g.mol./1000 g. From the solubilities quoted below for solutions containing NaCl and $LiNO_3$ calculate the activities of KIO_4 and plot the curve relating activity to ionic strength for the two "solvent salts". JONES and HECKMAN obtained the solubility of KIO_4 at zero ionic strength using the equation

$$\log m = \log m_0 + \frac{0 \cdot 5085\, I^{\frac{1}{2}}}{1 + 0 \cdot 3281\, a I^{\frac{1}{2}}} \cdot$$

m_{KIO_4}	m_{NaCl}	m_{KIO_4}	m_{LiNO_3}
0·02561	0·1024	0·02397	0·08075
0·02724	0·2025	0·02564	0·09282
0·03040	0·6096	0·02818	0·2089
0·03204	1·0289	0·03046	0·4112
0·03304	1·5394	0·03353	0·8179

IV-7.   BRØNSTED and LAMER (*J. Am. Chem. Soc.*, 1924, **46**, 555) determined by the solubility method the activity coefficient of oxalotetramminecobaltodithionate ($[Co(NH_3)_4C_2O_4]_2S_2O_6$) at 15 °C. Using the data given for the solubility in presence of K_2SO_4 and

$K_3Co(CN)_6$ evaluate the activity coefficient of $[Co(NH_3)_4C_2O_4]_2S_2O_6$ in solutions of the corresponding ionic strength.

	Added salt (equiv./l.)	Solubility (g.mol./l. . 10^4)
K_2SO_4	0·0	1·545
	0·0006	1·614
	0·0010	1·640
	0·0020	1·718
	0·0080	1·775
	0·0050	1·878
$K_3Co(CN)_6$	0·0010	1·651
	0·0020	1·728
	0·0050	1·889

IV-8.　If j is defined as $1 - \dfrac{\Delta T}{1 \cdot 858 \nu m_2}$ where ΔT is the depression of the freezing point of water when it is made m_2 molar with respect to an electrolyte dissociating into ν ions, show that the activity coefficient may be evaluated from

$$\ln f_{(m)_2} = \int_0^m (-j\, d\ln m_2) - j + \frac{5 \cdot 7 \cdot 10^{-4}}{\nu} \int_0^{\Delta T} \frac{\Delta T}{m_2}\, d(\Delta T)$$

(ΔC_P for the reaction $(H_2O)_s \rightleftarrows (H_2O)_l$ is 9 cals/g.mol.).

Hence evaluate the activity coefficient of KCl at 0·1, 0·5, 1·0 and 1·5m from the data of JONES and BURY (*Phil. Mag.*, 1927, [7], **3**, 1072) given below

m_2	ΔT	m_2	ΔT	m_2	ΔT
0·0988	0·340	0·6047	1·992	1·397	4·528
0·1246	0·425	0·7013	2·303	1·608	5·208
0·2381	0·808	0·8303	2·719	1·818	5·882
0·2998	1·007	1·020	3·328		
0·4549	1·511	1·220	3·960		

IV-9.　Show that if two aqueous solutions of different involatile

substances have the same vapour pressure, the activity coefficient of one ($f_{(m)_1}$) may be obtained from that of the other by the relation

$$\ln f_{(m)_1} = \ln f_{(m)_1} + \ln\left(\frac{m_1}{m_2}\right) + 2\int_0^{\sqrt{a_1}}\left(\frac{m_2}{m_1} - 1\right)\frac{d(\sqrt{a_1})}{\sqrt{a_1}}$$

ROBINSON and SINCLAIR (*J. Am. Chem. Soc.*, 1984, **56**, 1880) found that solutions of KCl and LiI of the following concentrations had the same vapour pressure.

m_{KCl}	m_{LiI}	m_{KCl}	$f_{(m)KCl}$
0·1235	0·1197	0·1	0·766
0·1714	0·1630	0·2	0·715
0·2034	0·1910	0·8	0·684
0·2819	0·2627	0·5	0·648
0·7848	0·6877	0·7	0·624
1·160	0·9705	1·0	0·602
1·834	1·098	1·5	0·581
1·825	1·443	2·0	0·572
2·586	1·906	2·5	0·569
2·854	2·089	3·0	0·570
2·974	2·170	3·5	0·573
8·245	2·327		
3·596	2·529		

Evaluate the activity coefficient of LiI in solutions from 0·1 to 2·5m.

IV-10.   It is found experimentally that the curve of $1 - f_0$ (where f_0 is the osmotic coefficient) against vm, for strong electrolytes at high dilutions, becomes asymptotic to the $1 - f_0$ axis as the concentration decreases. Show that this is in contradiction with the result expected from the classical theory. Although the $(1 - f_0) - vm$ curves for salts of the same valence type coincide, those for salts of different valence types do not. What particular fault in the classical theory does this fact suggest?

CHAPTER V

V-1.   Calculate the radius of the ionic atmosphere in solutions of $Al_2(SO_4)_3$ in 20% and 82% dioxan-water mixtures at 15 °C. and 45 °C. when the ionic concentration is 0·1, 0·01, 0·001, 0·0001 mol./l.

(For 20% Dioxan $\varepsilon = 64·01$ at 15 °C. and 54·88 at 45 °C.
     82% Dioxan $\varepsilon = 10·01$ at 15 °C. and 8·62 at 45 °C.).

V-2.   Show that in dilute solutions the ionic activity coefficients may be calculated from the mean activity coefficient of a salt by the equations

$$\log f_+ = \left(\frac{\nu}{\nu_+} - 1\right) \log f_\pm \, ,$$

$$\log f_- = \left(\frac{\nu}{\nu_-} - 1\right) \log f_\pm \, .$$

V-3.   Evaluate theoretically the mean activity coefficients for the complex salt in Question 7 Chapter 4 with addition of K_2SO_4.

V-4.   Show that the work done in charging $N_1 \ldots N_i$ ions of type $1 \ldots i$ having valence $z_1 \ldots z_i$ in a given solution is

$$w = -\Sigma \frac{N_i z_i^2 e_0^2 \varkappa}{3\varepsilon} \, .$$

Explain any difference between this expression and equation (20).

V-5.   Show that the osmotic coefficient of an electrolytic solution is given by

$$f_0 = 1 - \frac{e_0^3 \pi^{1/2} \Sigma N_i z_i^2}{3 (\varepsilon kT)^{1/2} \Sigma N_i} (\Sigma N_i z_i^2)^{1/2} \, .$$

V-6.   Using the result of Question 4 show that the heat absorbed when the concentration of a dilute solution of an electrolyte is reduced so that the solution is at infinite dilution, at constant pressure and temperature is

$$D_e = \frac{\Sigma N_i z_i^2 e_0^2 \varkappa}{2\varepsilon} \left[1 + \frac{T}{\varepsilon} \frac{\partial \varepsilon}{\partial T} + \frac{T}{3V} \cdot \frac{\partial V}{\partial T}\right] .$$

V-7. Show that the heat capacity of a dilute electrolytic solution $(C_p)_i$ is related to that of the solution at infinite dilution $(C_p)_0$ by

$$(C_p)_i = (C_p)_0 - \frac{\Sigma N_i z_i^2 e_0^2 \varkappa}{4\,\varepsilon T}\left[1 + \frac{2}{3}\frac{T}{V}\frac{\partial V}{\partial T} + \frac{2T}{\varepsilon}\frac{\partial \varepsilon}{\partial T} + \left(\frac{T}{V}\frac{\partial V}{\partial T}\right)^2 \right.$$

$$\left. + \left(\frac{T}{\varepsilon}\frac{\partial \varepsilon}{\partial T}\right)^2 + \frac{2T^2}{\varepsilon V}\frac{\partial V}{\partial T}\frac{\partial \varepsilon}{\partial T} - \frac{2}{3}\frac{T^2}{V}\frac{\partial^2 V}{\partial T^2} - \frac{2T^2}{\varepsilon}\frac{\partial^2 \varepsilon}{\partial T^2} \right].$$

V-8. Calculate to the nearest ångstrøm unit the minimum distance from the centre of the ion to which the condition $\dfrac{z_i e_0 \bar{\psi}}{kT} < 1$ can be considered to hold for a univalent ion in a 1 - 1 electrolyte and for a trivalent ion in a 8 - 1 electrolyte both at $0\cdot001M$ in aqueous solution at 25 °C. ($\bar{\psi}$ is the potential due to the ion and its ionic atmosphere).

V-9. The practical activity coefficients for NaCl in 1, 2, 8 and 4 molar solutions are $0\cdot655$, $0\cdot670$, $0\cdot719$ and $0\cdot791$ respectively. Calculate a mean value for the constant C in the HÜCKEL equation ($a = 4\cdot4 \cdot 10^{-8}$ cm.). What, approximately, is the absorption coefficient for nitrogen in a 2 molar sodium chloride solution at 25° if that for pure water at 25° is $0\cdot0142$?

V-10. Show that the distribution of a substance having permanent moment μ_A, and polarisability a_A about an ion of charge $z_i\varepsilon$ and radius a in a solvent of permanent moment μ_B and polarisability a_B is given, in solutions up to medium concentration, by the equation

$$N_r = N_0 \exp.\left[\frac{(a_A - a_B)(z_i e_0)^2}{2\,\varepsilon^2\,r^4\,kT}\left(\frac{e^{\varkappa(a-r)}\,(\varkappa r+1)}{(\varkappa a+1)}\right)^2 + \right.$$

$$\left. + \frac{(\mu_A\cos\theta_A - \mu_B\cos\theta_B)z_i e_0}{\varepsilon\,r^4\,kT}\left(\frac{e^{\varkappa(a-r)}\,(\varkappa r+1)}{(\varkappa a+1)}\right) \right].$$

CHAPTER VI

VI-1. CERNATASCU and MAYER (*Z. physikal. Chem.*, 1982, 160A, 817) measured the conductance of aqueous solutions of pure KAsO₂

and $NaAsO_2$ (Λ) and also of solutions of the same salt concentrations containing excess of $HAsO_2$ (Λ_r). Calculate the hydrolysis constants. ($\Lambda_{KOH} = 271 \cdot 5$ and $\Lambda_{NaOH} = 248 \cdot 1$).

	c (g.mol./l)	Λ	Λ_r
$NaAsO_2$	0·01562	84·0	79·30
	0·01018	86·38	80·84
	0·008294	89·14	82·30
	0·004161	92·00	84·49
$KAsO_2$	0·01018	110·3	105·31
	0·008295	111·64	106·05
	0·002080	120·00	110·00

VI-2.   100 cc. of $0 \cdot 01 N$ hydrochloric acid are titrated with N NaOH. Assuming complete dissociation of strong electrolytes and neglecting the volume change, plot the course of the specific conductance of the solution during titration.

$$(l_{\infty\,H^+} = 349 \cdot 82, \quad l_{\infty\,Na^+} = 50 \cdot 11, \quad l_{\infty\,Cl^-} = 76 \cdot 34, \quad l_{\infty\,OH^-} = 198).$$

VI-3.   MELCHER ($J.\ Am.\ Chem.\ Soc.$, 1910, 32, 54) measured the conductance of saturated aqueous $BaSO_4$ solutions at various temperatures. Show that the solubility of $BaSO_4$ may be represented by

$$\ln s_0 = -\frac{30{,}820}{RT} - \frac{42 \cdot 5}{R} \ln T - 66 \cdot 8.$$

$^{\circ} (°C.)$	$\varkappa$	Λ_0
18°	2·30 . 10^{-6}	123
25°	3·00 . 10^{-6}	144
50°	6·45 . 10^{-6}	229
100°	14·00 . 10^{-6}	434

VI-4.   GOLD ($Trans.\ Faraday\ Soc.$, 1948, 44, 506), followed the hydrolysis of acetic anhydride conductimetrically. In 10% acetone at 15 °C. the following results were obtained. Calculate the rate constant of the hydrolysis reaction.

(secs)	$c \cdot 10^4$ (Acetic acid)	t	$c \cdot 10^4$
84	3·27	784	17·27
176	5·51	965	19·78
276	7·96	1208	22·50
417	10·94	1431	24·58
601	14·36	10200 (∞)	34·01

VI-5. Using the experimental values of Question 2, Chap. IV calculate the true dissociation constants for nitric acid in ethyl and methyl alcohols.

VI-6. From the values given for the conductance of pure molten KNO_3 by JAEGER, (*Z. anorg. Chem.*, 1920, **113**, 27) and for the viscosity by DANTUMA, (*ibid*, 1928, **175**, 1), calculate the energies of activation associated with each of these processes.

Test WALDEN's rule and show that the form $\eta \Lambda^n = $ const. is required. Evaluate n.

$T\,^\circ C.$	$\varkappa$	ϱ (g./cc.)	$T\,^\circ C.$	η
346·1	0·653	1·863	348	0·02758
364·8	0·713	1·848	367	0·02480
385·2	0·776	1·833	386	0·02242
404·6	0·831	1·818	405	0·02043
418·4	0·876	1·807	418	0·01923
434·3	0·921	1·796	443	0·01712
452·4	0·973	1·781	450	0·01662
470·7	1·026	1·767	470	0·01531
500·4	1·108	1·745	492	0·01415
			530	0·01268

VI-7. Show that the equivalent conductance at infinite dilution of a long chain substance is related to the number (n) of volume elements composing the volume of its molecules by an equation of the form.

$$\log l_\infty = \text{const.} - x \log n$$

(*cf.* E. GONICK, *J. Phys. Chem.*, 1946, **59**, 291).

Assuming that the —CH_2— group is the unit volume element

evaluate the volume element equivalent of a —COO′ group and hence calculate l_{∞} for $C_{18}H_{36}(COO')_2$.

Acid	l_{∞}
Oxalic	75·6
Malonic	66·1
Succinic	59·7
Glutaric	55·8
Adipic	52·7
Pimelic	51·0
Suberic	48·9
Azelaic	45·5

VI-8.   Show that in a solution of a colloidal electrolyte (NaA), f, the proportion of sodium ion not associated with micelles, may be approximately given by

$$f = \frac{\Lambda}{(l_{Na})_{free} + l_A},$$

where Λ is the conductance of the solution, $(l_{Na})_{free}$ the mobility of the free sodium ions and l_A the mobility of the micelles, assuming that the micelles are of uniform size and each contains the same number of gegenions. ROBINSON and MOILLET (*Proc. Roy. Soc., A,* 1934, **143,** 630) measured the conductance and transport numbers (T_A) of solutions of "Meta dye". Calculate the proportion of bound Na^+ ions assuming that the mobility of the free sodium ions is the same as that of the sodium ions in equinormal solutions of (a) NaCl (b) Na_2SO_4.

Norm.	Λ	T_A	Norm.	NaCl		Na_2SO_4	
				n_+	Λ	n_+	Λ
			0·01	0·3918	118·51	0·3848	112·44
0·0891	51·5	0·681	0·02	0·3903	115·76	0·3836	106·78
0·02970	62·2	0·668	0·05	0·3878	111·06	0·3829	97·75
0·01367	72·1	0·624	0·10	0·3853	106·74	0·3829	89·98

VI-9.   GLEYSTEEN and KRAUS (*J. Am. Chem. Soc.,* 1947, **69,** 451) obtained the following values for the conductance of methyl tri-

n-butylamine chlorate in ethylene chloride at 25 °C.

$c \cdot 10^4$ (Mols/l.)	Λ_v
2·547	82·29
1·172	89·95
0·4866	48·75
0·2287	55·75

Evaluate the dissociation constant at the lowest and highest concentrations.

$$(\Lambda_0 = 68\cdot80, \quad \eta = 0\cdot00785, \quad \varepsilon = 10\cdot23)\ .$$

VI-10. Show from the ONSAGER equation for a weak electrolyte, $\Lambda_v = a\,(\Lambda_x - A\sqrt{ac}\,)$, that

$$\frac{F_{(z)}}{\Lambda} = \frac{c\,f^2\Lambda}{K\Lambda_\infty F_{(z)}} + \frac{1}{\Lambda_\infty}\,;$$

where f is the mean activity coefficient of the ions, and

$$F_{(z)} = 1 - z\,[\,1 - z\,\{1 - z\,(1 - z\ldots.)^{-1/2}\}^{-1/2}\,]^{-1/2},$$

$$\text{and}\quad z = \frac{A(c\Lambda)^{1/2}}{\Lambda_\infty^{1/2}}\ .$$

Given that

$$1 - z\,[\,1 - z\,\{1 - z\,(1 - z\ldots.)^{-1/2}\}^{-1/2}\,]^{-1/2}$$
$$= \tfrac{4}{3}\cos^2\tfrac{1}{3}\left[\cos^{-1}\left(-\frac{3\sqrt{3}(z)}{2}\right)\right]$$

evaluate the dissociation constant of methyl tri-n-butylamine perchlorate in ethylene chloride using the data of the previous problem.

CHAPTER VII

VII-1. The e.m.f. of the cell,

$$\text{Tl (55\% amalgam)} \ \bigg| \ \underset{\text{(sat.)}}{\text{TlCl}} \ \bigg| \ N\text{KCl} \ \bigg| \ \underset{\text{(sat.)}}{\text{Hg}_2\text{Cl}_2} \ \bigg| \ \text{Hg}\,,$$
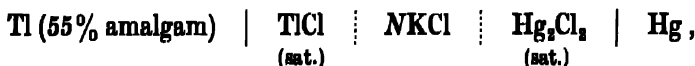
at $+25$ °C. is 0·729 v. The temperature coefficient of its e.m.f. is $+0\cdot00075$ v./°C. State the cell reaction and calculate the change in

heat content, and entropy accompanying this reaction. How much heat would be absorbed by the system if the reaction were carried out, (a) reversibly in a cell, (b) irreversibly in a calorimeter? Would $\left(\dfrac{\partial E}{\partial T}\right)_p$ remain constant as the temperature changed?

VII-2.   McINNES and PARKER (*J. Am. Chem. Soc.*, 1915, **37**, 1445) and BEATTIE (*ibid.*, 1920, **42**, 1128) determined the e.m.f.'s of the following cells,

     (A)   Ag │ AgCl, KCl ┊ KCl, AgCl │ Ag ;
                (sat.) c_1 c_2 (sat.)

     (B)   Ag │ AgCl, KCl │ K amalgam │ KCl, AgCl │ Ag .
                (sat.) c_1 c_2 (sat.)

c_1 (g.equiv./l.)	c_2 (g.equiv./l.)	E (cell A) (v.)	E (cell B) (v.)
0·05	0·005	—0·05473	—0·11085
0·1	0·01	—0·05400	—0·10893
0·5	0·05	—0·05357	—0·10740
1	0·1	—0·05290	—0·10655

Calculate the transport number of the potassium ion in these solutions. How is a simple procedure for this calculation justified in this particular system?

VII-3.   LEWIS and KEYES (*J. Am. Chem. Soc.*, 1918, **35**, 340) determined the e.m.f. of the cell,

       Li │ LiI in propylamine │ Li (0·0350% in Hg) ,

as +0·9502 v. at 25 °C.; and that of the cell,

Li (0·0350% in Hg) │ LiOH │ LiCl ┊ KCl ┊ KCl, Hg$_2$Cl$_2$ │ Hg ,
                      0.1m   0.1m   0.1m   1m   (sat.)
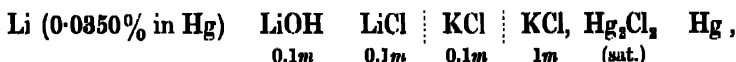
as +2·3952 v. at 25 °C.

Calculate the standard electrode potential of lithium if the mean ionic activity of LiOH in 0·1m aqueous solution is 0·074. (The equivalent conductances of 0·1m solutions are $\Lambda_{LiOH} = 204·4$, $\Lambda_{LiCl} = 97·9$, $\Lambda_{KCl} = 128·8$).

If the temperature coefficient of the e.m.f. of the first cell is +0·000822 v./°C., what is the differential heat of solution of Li in an 0·0350% amalgam?

VII-4. Comment on the degree with which saturated KCl suppresses liquid junction potentials by considering junctions between saturated KCl and N, $\dfrac{N}{10}$, and $\dfrac{N}{100}$ solutions of HCl and H_2SO_4 (saturated KCl is 4·7N; mobilities at infinite dilution may be used to give an approximate result).

VII-5. HILDEBRAND and RUHLE (*J. Am. Chem. Soc.*, 1927, **49**, 722) measured the e.m.f. of the cell,

$$Pb \mid PbCl_2 \text{ KCl} \mid Cl_2 .$$
(molten salts)

Calculate the activity coefficient of $PbCl_2$ in the mixed melt at 550° and 600° assuming that it is unity for the pure salt.

Mol fraction KCl	T °C.	E (v.
0	501	1·2690
	507	1·2650
	514	1·2604
	545	1·2382
	550	1·2382
	598	1·1980
	607	1·1930
0·05	534	1·2512
	553	1·2371
0·10	525	1·2620
	553	1·2417
	560	1·2357
	564	1·2330
0·20	540	1·2575
	560	1·2409
0·30	542	1·2754
	560	1·2618
	585	1·2411
	602	1·2266
	605	1·2246
0·40	560	1·2912
	610	1·2491

VII-6. LATIMER (*Oxidation Potentials*, 1988) suggests that for the dissolution of barium in acids the best value for the heat content change is, $\Delta H = -128,860$ cal./g.mol. and for the entropy change, $\Delta S = 18.4$ cal.deg.$^{-1}$mole^{-1}. Calculate the standard potential of barium. Suggest a possible electrode for the determination of barium ions in solution and calculate the value of its potential in any given solution of barium ions.

VII-7. POPOFF, RIDDIE, WIRTH and OUGH (*J. Am. Chem. Soc.*, 1931, **53**, 1195) measured the e.m.f. of the cell,

$$Pt\text{---}H_2 \mid HClO_4 \mathbin{\vdots} HClO_4 \; Hg(ClO_4)_2 \; Hg_2(ClO_4)_2 \mid Pt,$$
$$m \qquad m \qquad m_1 \qquad m_2$$
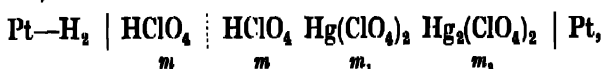
and gave values of the potential of the redox electrode with respect to a normal hydrogen electrode.

m	$m_1 = m_2$	E_H (v.)	m	$m_1 = m_2$	E_H
	mol./litre			mol./litre	
0·12	0·006	0·8356	0·04	0·006	0·8360
	0·004	0·8301		0·004	0·8325
	0·002	0·8211		0·002	0·8283
	0·001	0·8124		0·001	0·8148
	0·0005	0·8033		0·0005	0·8053
0·08	0·006	0·8362	0·02	0·001	0·8150
	0·004	0·8311		0·005	0·8063
	0·002	0·8221			
	0·0005	0·8042			

Calculate the standard redox potential of the mercuric, mercurous system.

VII-8. CROCKFORD and FARR (*J. Am. Chem. Soc.*, 1986, **58**, 87) measured the e.m.f.'s of cells of the type,

$$\text{(two phase)} \mid PbCl_2, \; Ba(NO_3)_2 \mathbin{\vdots} AgCl \mid Ag .$$
$$m_1 \qquad m_2 \qquad \text{(sat.)}$$
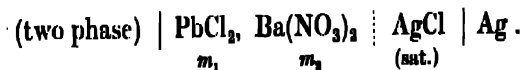
m_1	m_2	E (v.)
mol./litre	mol./litre	
0·01729	0·03575	0·51300
0·01647	0·03421	0·51331
0·01235	0·02564	0·52125
0·01097	0·02279	0·52480

m_1	m_2	E
0·008227	0·01709	0·58328
0·004112	0·008540	0·55416
0·002056	0·004720	0·57640
0·001028	0·002185	0·59940

Calculate the activity of $PbCl_2$ in these solutions.

VII-9. Calculate the standard potential of the azide electrode at 25 °C. (*cf.* STOUT, *Trans. Faraday Soc.*, 1945, **41**, 64) if the free energy of formation of gaseous HN_3 is $\Delta G = 78·5$ k.cal.mole^{-1} and the dissociation constant of aqueous HN_3 is $K = 2·8 \cdot 10^{-5}$. For the process of solution of HN_3 STOUT gives the values $\Delta H = -17·3$ k.cal.mole^{-1}, $\Delta S = -80$ cal.deg.$^{-1}$mole^{-1}. What would be the e.m.f. of a cell consisting a normal hydrogen electrode and a normal azide electrode at pressures of (a) 1 mm. of mercury and (b) 100 atm.?

VII-10. Calculate the standard potential of the magnesium electrode (*cf.* COATES, *J. Chem. Soc.*, 1945, 428) given the following data in joules per g.mol.

Entropies: (25 °C.)	Mg(c)	32·50 ;
(joule deg.$^{-1}$mole^{-1})	Mg(OH)$_2$(c)	68·13 ;
	H_2(g)	180·644 ;
	H_2O(l)	70·081 .

Standard heat contents: (25 °C.)

MgO(c)	—604,726 ;
H_2O(l)	—285,795 .

The heat content change for the reaction,

$$MgO + H_2O \rightarrow Mg(OH)_2 ,$$
$$\Delta H = -40,741 .$$
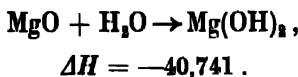
The free heat content change in the reaction,

$$H_2O(l) = H^+ + OH^- ,$$
$$\Delta G = 79,879 .$$
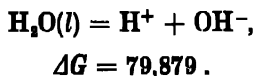
The solubility product of $Mg(OH)_2$ is $3·58 \cdot 10^{-12}$.

CHAPTER VIII

VIII-1. Suggest a system suitable for the electrometric titration of
0·01N KBr with $AgNO_3$. Plot the titration curve assuming that
the system is ideal and the volume remains constant.
$$(K_{s \, (AgBr)} = 5 \cdot 10^{-13}).$$

VIII-2. The e.m.f. of the glass electrode cell,

Ag   AgCl HCl   glass   HCl AgCl   Ag ,

     (sat.) $10^{-3}m$ $10^{-1}m$ (sat.)

is found to be 0·0605 v. at 25 °C. Calculate the asymmetry potential
of the glass assuming that both solutions are within the region
of the DEBYE-HÜCKEL limiting law.

VIII-3. GLASSTONE (*J. Chem. Soc.*, 1921, **119**, 1914) found that the
e.m.f. of the cell,

Pb $\mid$ PbO NaOH H_2 $\mid$ Pt ,

         1N 1 atm.

was 0·247 v. at 25 °C. If the e.m.f. of a cell composed of hydrogen
and oxygen electrodes both at atmospheric pressure and at 25 °C.
is 1·226 v. and the heat of dissociation of PbO is $\Delta H = 100,600$ cal.,
calculate approximately the temperature at which PbO will be
completely dissociated in the atmosphere. (Partial pressure of O_2
in the atmosphere is 0·21 atm.)

VIII-4. WYNNE-JONES (*Trans. Faraday Soc.*, 1936, **32**, 1397) measured
the ionic product of D_2O using the cell,

H_2 $\mid$ KCl $\vdots$ KCl $\mid$ KCl $\mid$ H_2

     m_1 HCl   Sat. m_2 NaOH

$m_1 = m_2$ (mole/litre)	I (ionic strength in each compartment)	T °C.	E (v.)
0·0057	0·1003	15	0·5990
		25	0·5976
		35	0·5968
0·0049	0·0855	15	0·5921
		25	0·5908
		35	0·5900

$m_1 = m_2$	I	T	E
0·0024	0·0422	15	0·5578
		25	0·5554
		85	0·5582

Taking the dielectric constant of D_2O as approximately 0·986 that of H_2O at the same temperature, calculate the ionic product and the heat of ionisation of D_2O.

VIII–5.   WAITKINS and McCROSKY (*J. Am. Chem. Soc.*, 1946, **68**, 1885) measured the e.m.f. at 25° of the cell,

$$\text{Ag} \mid \text{AgSeCN, KSeCN} \mathbin{\vdots} \text{KNO}_3 \mathbin{\vdots} \text{AgNO}_3 \mid \text{Ag}.$$
$$\text{(sat.)} \qquad m_1 \qquad \text{Sat.} \qquad m_2$$

m_1 mol./litre	m_2 mol./litre	E (v.)
0·0894	0·1363	0·7081
0·0985	0·0856	0·7008
0·0958	0·3183	0·7288
0·0644	0·1340	0·6988

Activity coefficients

m mol./litre	$AgNO_3$	KI	KBr
0·005	0·925	0·928	0·927
0·01	0·897	0·904	0·908
0·02	0·860	0·874	0·879
0·05	0·793	0·823	0·836
0·1	0·724	0·777	0·790
0·2	0·640	0·727	0·780
0·5	0·499		

Taking the activity coefficient of KSeCN as the mean of those of KBr and KI at the same concentration calculate the solubility product of AgSeCN.

VIII–6.   FERRAL, RIDGION and RILEY (*J. Chem. Soc.*, 1986, 1121) measured the e.m.f. of the cell,

$$\text{Zn} \mid 0{\cdot}01M \ \text{ZnSO}_4 \mathbin{\vdots} 0{\cdot}01M \ \text{ZnSO}_4 + \text{CH}_2\text{NH}_2\text{COONa} \mid \text{Zn}.$$

$m_1 \cdot 10^3$ mol./litre	E (v.)	$m_1 \cdot 10^3$ mol./litre	E (v.)
11·5	0·018	72·7	0·225
17·0	0·042	100·0	0·246
22·2	0·094	123·5	0·258
32·1	0·153	150·0	0·267
50·0	0·197	180·0	0·276

If the activity of $0\cdot01M$ ZnSO$_4$ is 0·00633 find the simplest complex ion which appears to exist in the solution of ZnSO$_4$ and NH$_2$CH$_2$COONa, and calculate the dissociation constant of this complex.

VIII–7. An $N/20$ solution of 1 : 4-naphthoquinone was titrated with $N/30$ TiCl$_3$, both solutions being N with respect to HCl and made up using 50% aqueous ethanol as solvent.

The e.m.f. between a platinum electrode in the solution being titrated and a calomel electrode was measured. The calomel electrode potential was found to be $+0\cdot2531$ on the hydrogen scale in the solvent used. Calculate the formal redox potential of 1 : 4-naphthoquinone.

V ml. TiCl$_3$ solution added	E (v.)	V ml. TiCl$_3$ solution added	E (v.)	V ml. TiCl$_3$ solution added	E (v.)
0·25	0·2639	8·0	0·2283	15·5	0·1890
0·75	0·2585	9·0	0·2255	16·0	0·1819
1·00	0·2575	10·0	0·2222	16·5	0·1521
2·00	0·2480	11·0	0·2190	17·0	0·0888
3·0	0·2450	12·0	0·2168	17·5	—0·0496
4·0	0·2411	13·0	0·2120	18·0	—0·1680
5·0	0·2378	14·0	0·2061	19·0	—0·1880
6·0	0·2350	14·5	0·2009	20·0	—0·1943
7·0	0·2318	15·1	0·1982		

VIII–8. 50 ml. of an aqueous solution of acetic acid were titrated with $0.221N$ NaOH at 19 °C using a cell consisting of a quinhydrone electrode and a normal calomel electrode. Calculate the thermodynamic dissociation constant of acetic acid. (The standard e.m.f. of the cell at the temperature of the experiment is $0\cdot4206$ v.).

ml. NaOH solution added	E (v.)	ml. NaOH	E (v.)
0·00	0·2882	9·0	0·0981
1·0	0·2012	10·0	0·0472
2·0	0·1819	10·2	0·0088
3·0	0·1696	10·3	—0·0420
4·0	0·1595	10·4	—0·0648
5·0	0·1491	10·5	—0·0777
6·0	0·1396	11·0	—0·1034
7·0	0·1284	12·0	—0·1272
8·0	0·1160		

VIII-9.   Show that the dissociation constants of a dibasic acid are related by the equation,

$$\frac{a_H \cdot L f_2}{N} = K_1 \frac{a_H \cdot M f_2}{N f_1} = K_1 K_2 ;$$

where f_1, f_2 are the DEBYE-HÜCKEL activity coefficients for a univalent and a divalent ion respectively, the activity of an uncharged molecule being taken as equal to its concentration;

$$L = b + a_{H^+} - [OH^-] ,$$
$$M = a - b - a_{H^+} + [OH^-] ,$$
$$N = 2a - b - a_F \quad [OH^-] ;$$

a is the initial total concentration of the acid and b is the concentration of the cations of the base with which the solution is being titrated.

SPEAKMAN (*J. Chem. Soc.*, 1940, 855) titrated 40 cc. of $0·000793m$ adipic acid with $0·0194m$ NaOH at 20 °C. and measured the pH of the solution during the titration. Calculate the dissociation constants of adipic acid using his measurements given below.

ml. NaOH solution added	pH	ml. NaOH	pH
0·726	4·82	1·769	4·99
0·944	4·47	2·281	5·35
1·397	4·76	2·462	5·48
1·582	4·88		

VIII-10. Show that in a solution of $MgCl_2$ being titrated with $Ba(OH)_2$ solution,

$$[MgOH^+] = 2[Ba^{++}] + [H^+] - [OH^-] - [HCO_3^-] - 2[CO_3^-],$$

assuming that under the experimental conditions used no $Mg(OH)_2$ is formed.

STOCK and DAVIES (*Trans. Faraday Soc.*, 1948, **44**, 856) titrated 854·4 g. of a solution containing 0·02959 g.mol. $MgCl_2$ per 1000 g. with a $Ba(OH)_2$ solution containing 0·04654 g.equiv. $Ba(OH)_2/1000$ g. at 25 °C. The specific conductivity of the water used for the $MgCl_2$ solution was $0·65 . 10^{-6}$ohm.$^{-1}$cm.$^{-1}$ (assumed all due to CO_2). Calculate the second dissociation constant of $Mg(OH)_2$.

g. $Ba(OH)_2$ solution added	pH
0·1155	8·06
0·2110	8·40
0·6215	8·95
1·0030	9·24

The dissociation constants of carbonic acid are

$$K_1 = 4·45 . 10^{-7}, \quad K_2 = 5·7 . 10^{-11},$$

and appropriate ionic activity coefficients may be obtained using the equation

$$\log f = - 0·5 z^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0·20 I \right)$$

CHAPTER IX

IX-1. MOELLER (*J. Phys. Chem.*, 1946, **50**, 242) studied the hydrolysis of the rare earth sulphates. Calculate the hydrolysis constants for cerium and yttrium sulphates assuming the reactions to be

$$R^{+++} + H_2O \rightleftarrows ROH^{++} + H^+,$$

or $$R^{+++} + H_2O \rightleftarrows RO^+ + 2H^+.$$
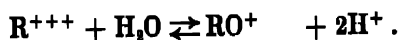
Which mechanism appears more probable?

		pH	
c (g.mol/l)	Ce		Y
0.100	5.00		8·88
0·075	5·05		8·49
0.050	5·15		8·68
0·010	5·65		4·85
0·005	5·80		5·00

IX-2.   GOLDSCHMIDT and MATHIESEN (*Z. physikal. Chem.*, 1926, **119**, 489) give the following values of dissociation constants of positively charged acids. Test equation (56) using this data and evaluate the intrinsic strength of these acids.

	Ethanol	Methanol	Water
Aniline	$2 . 10^{-6}$	$1 . 10^{-6}$	$2·4 . 10^{-5}$
o-Toluidine	$2·5 . 10^{-6}$	$1·2 . 10^{-6}$	$4 . 10^{-5}$
m-Toluidine	$1·3 . 10^{-6}$	$6·1 . 10^{-7}$	$2·1 . 10^{-5}$
p-Toluidine	$5·4 . 10^{-6}$	$2·8 . 10^{-7}$	$6·9 . 10^{-6}$
p-Chloraniline	$2·2 . 10^{-5}$	$1·2 . 10^{-5}$	$1·2 . 10^{-3}$
α-Picoline	$2·9 . 10^{-6}$	$5·7 . 10^{-7}$	$2·6 . 10^{-6}$
β-Picoline	$1·3 . 10^{-6}$	$8 . 10^{-7}$	$1·2 . 10^{-6}$
sym-Collidine	$9·1 . 10^{-8}$	$1·9 . 10^{-8}$	$5 . 10^{-8}$
Quinaldine	$3·4 . 10^{-6}$	$8·6 . 10^{-7}$	$3 . 10^{-6}$
Imidazole	$2 . 10^{-8}$	$7·3 . 10^{-9}$	$1 . 10^{-7}$
Pyridine	$1·9 . 10^{-5}$	$2·9 . 10^{-6}$	$5·7 . 10^{-6}$

Use the pyridinium ion as a standard.

(Ethanol, $\varepsilon = 25$; Methanol, $\varepsilon = 31$).

IX-3.   MASI and KNIGHT (*J. Am. Chem. Soc.*, 1945, **67**, 1558) measured the e.m.f. at 25 °C. of the cell,

Pt, H$_2$ | HCl   , AgCl | Ag .
(1 atm.)   in 20% ethylene glycol-water   (sat.)

containing thymol blue indicator. The fraction of indicator in the basic form (x) was determined optically.

c_{Cl^-} (equiv./litre)	E (v.)	x
0·00163	0·54306	0·075
0·00658	0·47409	0·238
0·02204	0·41561	0·482
0·05949	0·36774	0·696

Calculate the indicator constant and suggest the range in which the indicator could be used in 20% ethylene glycol (constants for equation V—51. $A = 0.5701$, $B = 3.418 . 10^6$, $a = 4 . 10^{-8}$, $C = 0.135$).

IX-4. What ratio would be expected from a simple statistical viewpoint between the first dissociation constant of a symmetrical dibasic acid and the dissociation constant of its monoethyl ester?

IX-5. Show that the buffer capacity of a weak acid of dissociation constant K_A at a concentration c_0 with addition of a strong base (concentration in solution c_B) is given by

$$\frac{dc_B}{dpH} = 2 \cdot 303 \left\{ \frac{c_0 \, K_A \, [H^+]}{(K_A + [H^+])^2} + [H^+] + [OH^-] \right.$$

Hence, evaluate the pH at which such a solution is the most effective buffer.

What does the above expression become if the acid is strong? In which regions does a strong acid solution act as an effective buffer?

IX-6. If a weak acid (HA_1) is dissociated to an extent α in a solution in which its concentration is m_1, show that its degree of dissociation α' when a second acid of dissociation constant K_2 is added, so that concentration of the second acid is m_2, may be found from the relation

$$\alpha' = \alpha \left(1 + \frac{K_2 \, m_2}{K_1 \, m_1} \right)$$

If a base is added to the solution so that its concentration is m_B and a fraction φ reacts with the first acid show that the ratio of the acid dissociation constants is given by

$$\frac{K_1}{K_2} = \frac{\varphi}{1-\varphi} \frac{\left\{ m_2 - m_B \left(1-\varphi\right) \right\}}{\left(m_1 - m_B\,\varphi\right)}.$$

IX-7. BRANCH and MYAMATO (*J. Am. Chem. Soc.*, 1930, **52**, 868) measured the pH at half neutralisation point of glycine and alanine titrated with $0.1N$ acid and $0.1N$ base. The amino acids were initially in $0.02N$ solution.

	Temp.	pH (half equiv. of base added)	pH (half equiv. of acid added)
Glycine	0°	10·315	2·575
	20°	9·724	2·587
Alanine	0°	10·464	2·575
	20°	9·825	2·587

Calculate the protolytic equilibrium constants K_1 and K_2 and also the heat content changes for the corresponding reactions.

IX-8. OWEN (*J. Am. Chem. Soc.*, 1934, **56**, 24) obtained values for the e.m.f. of the cell,

Pt | H$_2$ | Glycine, Glycine hydrochloride, AgCl | Ag ,
(1 atm.) m_1(mol./l.) m_2(mol./l.)   (sat.)

at 20 °C.

$m_2 . 10^6$	E (v.)	
5126	0·52135	
6449	0·51376	
8488	0·50450	$\dfrac{m_1}{m_2} = 1·1801$
14107	0·48890	
27022	0·47043	
37740	0·46203	

Values were also obtained for the e.m.f. of the cell,

Pt | H$_2$ | Glycine, Sodium Glycinate, NaCl, AgCl | Ag .
(1 atm.) m_1(mol./l.) m_2(mol./l.) m_3(mol./l.) (sat.)

$m_3 . 10^6$	E (v.)	
4659	0·93651	
5477	0·93264	$\dfrac{m_1}{m_2} = 1·0187$
8627	0·92132	
28135	0·89747	
34488	0·88779	$\dfrac{m_2}{m_3} = 0·98487$
50907	0·87880	

Calculate the constants K_1 and K_2 and compare with those obtained from the previous question.

IX-9. GANE and INGOLD (*J. Chem. Soc.*, 1928, 1594) give the following values for the dissociation constants of dibasic acids at 20 °C.

	$K_1 . 10^6$	$K_2 . 10^5$
Malonic	177·0	4·87
Succinic	7·36	4·50
Glutaric	4·60	5·34
Adipic	8·90	5·29
Pimelic	3·80	4·87
Suberic	8·07	4·71
Azelaic	2·82	4·64

Calculate the distance between the carboxyl groups in these acids. What types of structure does this suggest? What structure would be expected for β-n-propyl glutaric acid if its dissociation constants are $K_1 = 4·97 . 10^{-5}$, $K_2 = 4·32 . 10^{-7}$?

IX-10. KOSSIAKOFF and HARKER (*J. Am. Chem. Soc.*, 1938, 60, 2047) showed that the free heat content of ionization (ΔG) of an oxy-acid could be represented by

$$\Delta G = w + RT \ln \frac{n_0}{n_H} + C ;$$

where C is a constant and $\dfrac{n_0}{n_H}$ is a symmetry term, n_0 being the number of equivalent oxygen atoms not bonded to hydrogen in the acid ion and n_H the number of equivalent hydrogen atoms in the acid molecule. Show that w, the electrostatic work of transfer of the proton from the position in the acid (1) to a water molecule (2) is

$$w = \sum_j \frac{q_j \, e_0}{\varepsilon} \left(\frac{1}{(r_j)_1} - \frac{1}{(r_j)_2} \right) ,$$

where r_j is the distance of the proton from a point of the molecule having "formal charge" q_j (Nuclear charge — number of electrons). The ionisation constant of phosphoric acid is $10^{-2·1}$. Calculate the value of the constant C. Hence calculate the ionisation constant of H_3AsO_4 and by calculation of ionisation constant of

germanic acid decide whether its structure is H_2GeO_3 assuming a symmetrical planar distribution of Ge—O bonds or is H_4GeO_4 with a tetrahedral structure. The experimental value for germanic acid is log $K = -8.6$.

The O_{acid}—H—O_{water} distance is 2·70 Å, the O—H bond length is 0·95 Å, and the X—O—H bond angle is 110°. The X—O bond length is 1·53 Å for P, 1·66 Å for As, and 1·59 Å for Ge. The dielectric constant in the neighbourhood of the ion may be taken as 3·0 (following DEBYE, *Polar Molecules*, 1929).

CHAPTER X

X-1.   The variation of the interfacial tension of the interface Hg | N KCl — H_2O with potential was measured using a drop weight method (PARSONS, *unpublished*). Calculate the capacity of the electrode double layer, in the potential range given, by graphical differentiation.

$\psi_{(H_2)}$ (v.)	γ (dyne/cm.)	$\Delta\psi_{(H_2)}$ (v.)	γ (dyne/cm.)
+0·242	867·4	—0·540	412·0
+0·150	887·0	—0·640	402·0
+0·062	402·0	—0·740	390·7
—0·040	414·7	—0·845	376·7
—0·150	422·4	—0·945	362·0
—0·205	424·0	—0·995	344·0
—0·278	424·9	—1·140	325·2
—0·350	423·0	—1·255	301·8
—0·440	418·5		

X-2.   If γ_1, γ_2 and γ_3 are the interfacial tensions of a mercury-solution interface when the applied potential difference is $\Delta\psi - a$, $\Delta\psi$ and $\Delta\psi + a$ respectively, show that, approximately,

$$\frac{\partial^2\gamma}{\partial\Delta\psi^2} = \frac{\gamma_1 + \gamma_3 - 2\gamma_2}{a^2}.$$

Comment on the validity of this expression and check it by recalculating the capacity of the system in Question 1 by means of it. Calculate the capacity of a mercury electrode in pure

N KNO$_3$ solution and in the same solution which has been made $M/10$ with respect to tertiary amyl alcohol using the data of Gouy (*Ann. Chim. Phys.*, 1906, (8), 8, 291) given.

Compare the ratio of the capacities at 1·2 v. with that of the dielectric constants of water (78) and amyl alcohol (16). To what conclusion does this lead?

$\Delta\psi$(v.)	γ'_{KNO_3}	$\gamma'_{KNO_3 + AmOH}$	$\Delta\psi$(v.)	γ'_{KNO_3}	$\gamma'_{KNO_3 + AmOH}$
0·3	860·8	860·3	1·1	979·1	982·9
0·4	897·4	896·5	1·2	964·2	925·1
0·5	927·2	926·2	1·3	944·2	916·6
0·6	951·6	949·6	1·4	919·7	905·5
0·7	970·6	952·3	1·5	891·2	887·2
0·8	983·4	949·4	1·6	858·8	857·2
0·9	989·4	944·8	1·7	822·6	822·1
1·0	988·0	939·3	1·8	782·7	782·0

Note: The γ' of Gouy is in units relative to the Hg—pure water interfacial tension which is taken as 1000 units. The interfacial tension of the Hg—pure water interface is 426·7 dynes/cm.

X-3.   Mercury is allowed to stream into a N KCl solution. The stable length of the Hg stream is 9·60 cm. and its diameter is 0·0144 cm. The rate of transfer of mercury is 0·0553 cm.^{3}sec.$^{-1}$. The electrode requires a current of $1·07 . 10^{-4}$ amps to maintain it at a potential of —0·586 v. with respect to a normal hydrogen electrode. No current is required to keep it at a potential of —0·280 v.

Calculate the electrode capacity.

X-4.   Check the relation $\zeta = \text{const.} + \dfrac{RT}{F} \ln c_{H^+}$, by calculating the ψ_1 values for an electrode potential of —0·5 v. in 0·001, 0·01 and 0·1N HCl at 25 °C. using the Stern equation, assuming that specific adsorption is negligible (ε in the diffuse double layer $= 40$, $C = 20\mu F/$cm.^{2} and $\delta = 3 \cdot 10^{-8}$ Å).

X-5.   A mercury electrode is polarised at a constant c.d. of $3 . 10^{-6}$ amp.cm.$^{-2}$ in pure $N/100$ aqueous HCl. The potential of this electrode is —1·003 v. with respect to a normal calomel electrode

(liquid junction potentials being suppressed). When the solution is made $10^{-6}N$ with respect to lanthanum chloride the potential becomes —1·010 v., and when it is made $10^{-4}N$ with respect to LaCl₃ the potential becomes —1·066 v. LEVINA and SARINSKY (*Acta Physicochim.*, *U.R.S.S.*, 1937, **7**, 485) suggested that this change was due to an alteration in the structure of the double layer, and was equal, and opposite in sign, to the change in the ψ_1 potential. Test this hypothesis by calculating the ψ_1 potential for an Hg electrode under the above conditions using STERN's theory, neglecting specific adsorption potentials. (The "absolute" potential of the normal calomel electrode is +0·500 v.)

X-6.   The adsorption of a capillary active substance at a mercury electrode causes a lowering of the mercury-solution interfacial tension. Using the data given in Question 2 plot the decrease of interfacial tension, due to the presence of amyl alcohol, against potential (an adsorption curve).

By considering the energy of a dipole in an electric field, show that the surface tension lowering may be represented by

$$\varDelta\sigma = \varDelta\sigma_0 \, e^{-(a\varDelta\psi' - b\varDelta\psi)} \,,$$

or

$$\varDelta\sigma = \varDelta\sigma_{max.} \, e^{-a(\varDelta\psi - \varDelta\psi_{max.})'} \,.$$

assuming that the surface tension lowering caused by a component is proportional to the surface excess of that component, and that the field strength near the electrode surface is proportional to the potential of the electrode.

Obtain values of the parameters $\varDelta\sigma_{max.}$ the maximum surface tension lowering, $V_{max.}$ the potential at which this occurs, and the constant a, for $M/10$ *tert.*-amyl alcohol in N KNO₃.

X-7.   It has been suggested that the ζ potential measured by electro-phoresis $\left(\zeta_e = \dfrac{4\pi\eta u}{\varepsilon}\right)$, differs from that calculated from electro-osmosis experiments $\left(\zeta_0 = \dfrac{4\pi\eta u l}{\varepsilon\varDelta\psi q}\right)$, u is the linear velocity through the plug in a closed system type of experiment). This hypothesis can be tested using a substance such as octadecyl

alcohol, which may be prepared both in the form of colloidal particles, and in the form of a porous plug.

The following results were obtained in an experiment of this type:

pH	u (cm./sec.)	t (sec.)
2	$3\cdot39 \cdot 10^{-4}$	590
4	$4\cdot67 \cdot 10^{-4}$	358
6	$9\cdot17 \cdot 10^{-4}$	144
8	$2\cdot02 \cdot 10^{-3}$	90·5
10	$2\cdot52 \cdot 10^{-3}$	84·7

(u is the velocity of transference through a plug of octadecyl alcohol having $q/l = 0\cdot0917$ cm. The potential difference between the electrodes on either side of the plug was maintained at 100 v. t is the mean time required for a particle of octadecyl alcohol to move 1 mm. along a uniform tube containing electrodes 2·86 cm. apart, the potential difference across the electrodes being 10 v.).

Test the above hypothesis by calculating the ratio ζ_s/ζ_0.

X-8.   Show that the potential difference between two electrodes, area A, one l cm. above the other, in a medium of density ϱ, viscosity η, and of conductance $\varkappa$, in which n spherical particles, radius r, density ϱ', and surface charge density q, are falling under the influence of gravity is

$$\Delta\psi = \frac{8\,\pi\,r^4\,n\,q\,g\,l\,(\varrho'-\varrho)}{9\,\eta\,A\,\varkappa}$$

X-9.   The osmotic pressure of a protein solution inside a membrane in contact with an ionic solution may be written as

$$\Delta\pi = \Delta\pi_i + \Delta\pi_p,$$

where $\Delta\pi_i$ is the osmotic pressure due to the ions inside the membrane and $\Delta\pi_p$ is that due to the protein.

Show that

$$\Delta\pi_i = RT \int_0^\infty c_p \, d\ln a_p;$$

$$\Delta\pi_i = RT \int_0^u c_p \, n_p \, du,$$

where c_p is the protein concentration, and a_p its activity, n_p is

the mean valency of the protein, and $u = \dfrac{\Delta\psi_m F}{RT}$ where $\Delta\psi_m$ is the membrane potential. Calculate $\Delta\pi_p$ from the measurements of ADAIR (*Proc. Roy. Soc.*, 1929, **126**, 16) for haemoglobin (valency 8·5) at 0 °C.

c_p (mols/litre)	$\Delta\psi_m$ (millivolts)	$\Delta\pi$ (mm./Hg) (observed osmotic pressure)
0·000103	— 0·02	1·9
0·000555	— 0·10	11·2
0·001320	— 0·28	28·8
0·00357	— 0·75	103·6
0·00493	— 1·10	179·0

X-10.   RUTGERS (*Trans. Faraday Soc.*, 1940, **36**, 69) pointed out that if the surface conductance of a capillary used in streaming potential measurements is $\varkappa_w$ the measured ζ potential calculated from equation (53) (ζ_i) is not the true ζ-potential (ζ).

Show that
$$\zeta = \zeta_i\left(1 + \frac{2\,\varkappa_w}{r_i\,\varkappa_0}\right)$$

where $\varkappa_0$ is the conductance of the liquid and r_1 is the radius of the tube. Hence show that the true ζ potential may be calculated from measurements using capillaries of different radii (r_1 and r_2). Calculate the true ζ potential in solutions of KCl from the data of RUTGERS who used glass capillaries radius $r_1 = 0\cdot011$ cm., $r_2 = 0\cdot039$ cm.

$c \cdot 10^6$ (mol./l.)	$\varkappa_0$ ohm^{-1}cm.$^{-1}$	ζ_1 (mv.)	ζ_2 (mv.)
2	10·5 . 10^{-7}	—75	—148
6	16·3 . 10^{-7}	—85	—139
20	35·2 . 10^{-7}	—91	—134
40	57·5 . 10^{-7}	—94	—127
80	135 . 10^{-7}	—95	—121

Calculate also the surface conductance of the capillaries.

CHAPTER XI

XI-1. The hydrogen overpotential at a mercury cathode in 50%
aqueous methyl alcohol made $N/10$ with respect to HCl was
measured by Bockris and Parsons (*Trans. Faraday Soc.*,
1949, **45**, 916) whose measurements are given below.

i amp.cm.$^{-2}$	η volt
10^{-6}	—0·665
$3 . 10^{-6}$	—0·716
10^{-5}	—0·791
$3 . 10^{-5}$	—0·834
10^{-4}	—0·893
$3 . 10^{-4}$	—0·937
10^{-3}	—0·988
$3 . 10^{-3}$	—1·031
10^{-2}	—1·089
$3 . 10^{-2}$	—1·122

Calculate the Tafel constants a and b and the exchange current
in this system.

XI-2. Machu (*Korrosion und Metallschütz*, 1937, **13**, 1) has suggested
that the change in overpotential at an iron cathode due to the
addition of a corrosion inhibitor is caused by a decrease in the
concentration of the depositing ion caused by the presence of
the inhibitor. Bockris and Conway (*J. Phys. and Colloid Chem.*,
1949, **53**, 527) observed that at 10^{-3} amp.cm.$^{-2}$ the hydrogen
overpotential on iron was 0.35 v. while on the addition of 10^{-1}
mol./l. of acridine it rose to 1·57 v. How does this result agree
with the theory of Machu?

XI-3. The hydrogen overpotential at a dropping mercury electrode
at $2 . 10^{-4}$ amp.cm.$^{-2}$ in $N/100$ aqueous HCl was found to be
0·05 v. higher than that expected, from extrapolation of results
at lower current densities, after correction for potential drop in
the solution (Parsons, *Thesis*, London, 1948). Can this result be
accounted for by concentration polarisation? (Diffusion coefficient

of $H^+ = 9\cdot84 \cdot 10^{-5}$; drop time of electrode $1\cdot86$ secs; rate of mercury flow $7\cdot8$ mg./sec.; Transport number of $H^+ = 0\cdot84$.)

XI-4. Show that the time required to reach a system of weight fraction of bismuth (q) in the electrolysis of B g. of $BiCl_3$ is

$$t = \frac{8\,q\,B\,F}{a\,A_w\,I\,\{1 + (c-1)\,q\}}$$

where F is the Faraday, a is the current efficiency, I is the current passed through the cell, A_w is the atomic weight of Bi and c is the ratio of the molecular weight of $BiCl_3$ to the atomic weight of Bi.

It is known that in the system Bi—$BiCl_3$ the liquid splits into two phases at $850°$ when the weight fraction of bismuth is greater than 29%. 100 g. of $BiCl_3$ were electrolysed with a current of 2 amps. The liquid remained homogeneous for $8\cdot32$ hours. Calculate the mean current efficiency during this time.

XI-5. The following values were obtained by Bockris and Parsons (*Trans. Faraday Soc.*, 1949, **45**, 916) for the overpotential at a mercury cathode in $N/10$ HCl solution in pure methanol. Calculate the mean heat of activation of the electrode process at the reversible potential.

c.d.	η volts at T °C.				
(amp.cm.$^{-2}$)	$1\cdot9$ °C.	$12\cdot3$ °C.	$20\cdot5$ °C.	$80\cdot4$ °C.	$89\cdot5$ °C.
10^{-5}	—$0\cdot737$	—$0\cdot691$	—$0\cdot676$	—$0\cdot650$	—$0\cdot638$
$3 \cdot 10^{-5}$	—$0\cdot793$	—$0\cdot759$	—$0\cdot739$	—$0\cdot710$	—$0\cdot689$
10^{-4}	—$0\cdot842$	—$0\cdot818$	—$0\cdot797$	—$0\cdot768$	—$0\cdot746$
$8 \cdot 10^{-4}$	—$0\cdot890$	—$0\cdot872$	—$0\cdot840$	—$0\cdot817$	—$0\cdot800$
10^{-3}	—$0\cdot944$	—$0\cdot928$	—$0\cdot891$	—$0\cdot864$	—$0\cdot852$

XI-6. Hickling and Salt (*Trans. Faraday Soc.*, 1942, **38**, 474) have suggested that hydrogen overpotential is caused by the presence of atomic hydrogen gas, the electrode acting effectively as an atomic hydrogen electrode. If the free heat content change for the reaction, $2H \rightarrow H_2$, $\Delta G = -91,460$ cal.mole^{-1} calculate the pressure of atomic hydrogen which would cause an overpotential of $1\cdot04$ v. Assuming that the atoms occupy a layer of solution 100 Å thick

calculate the number present per cm². Calculate the velocity of the atoms required to give the calculated apparent concentration if the current density required for an overpotential of 1·04 v. is 10^{-3} amp.cm.$^{-2}$ (e.g. Hg cathode).

XI-7. If the solution adjacent to a mercury cathode evolving hydrogen is made $6 \cdot 10^{-5}$ molar with respect to arsenic oxide the variation of cathode potential with current density is as follows (BOCKRIS and PARSONS *unpublished*).

c.d. (amp.cm.$^{-2}$)	e_{H_2} (volts)
10^{-6}	—0·14
$3 \cdot 10^{-6}$	—0·16
10^{-5}	—0·22
$3 \cdot 10^{-5}$	—0·35
10^{-4}	—0·38
$3 \cdot 10^{-4}$	—0·41
10^{-3}	—0·70
$3 \cdot 10^{-3}$	—1·03
10^{-2}	—1·11

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that the half-wave potential of the reactions $As^{+++} \to As$ and $As \to AsH_3$ were —0·20 v. and —0·44 v. in $N/10$ HCl. Compare these results by plotting the experimental and calculated V—log i curves. (Diffusion coefficient of As^{+++} may be taken as 10^{-5} cm.²sec.$^{-1}$. Assume the experimental value for the first limiting current.)

XI-8. Show that if deposition continues at a rate corresponding to the potential of the electrode the decay of overpotential after the external circuit has been interrupted is given approximately by

$$e = \frac{RT}{aF} \ln \frac{aF}{RT} \cdot \frac{i_0 t}{C},$$

where t is the time elapsed after interrupting the circuit, i_0 is the exchange current and C the capacity of the electrode double layer. BUTLER and ARMSTRONG (*Trans. Faraday Soc.*, 1933, **29**,

1261) obtained the following results for a mercury electrode in aqueous acid solution.

t (secs)	e_{H_2}
10	—0·560
20	—0·525
80	—0·505
50	—0·479
75	—0·458
100	—0·450
150	—0·430
200	—0·415

Test the derived relation and evaluate C if $i_0 = 10^{-12}$ amp.cm.$^{-2}$.

XI-9.   The rate of increase of thickness of a corrosion film, e.g. an oxide film, due to the passage of ions through the continuous lattice of the film would be expected to follow the law

$$\frac{dy}{dt} = \frac{k}{y} \, ,$$

where y is the thickness and k is a constant.

Assuming that the film consists of an electronic and an electrolytic conductor in series and that its total specific conductance is $\varkappa$ (the transport numbers of the electrons, cations and anions being n_e, n_c and n_a respectively) show that the constant k is given by

$$k = -\frac{W \varkappa n_e (n_c + n_a) \Delta G}{z \varrho F^2} \, ,$$

where W is the equivalent weight, ϱ the density and ΔG the free energy of formation of the film substance; z is the valency of the corroding metal and F is the Faraday.

XI-10.   Assuming that the equivalent conductance (Λ) of a 1 : 1 electrolyte is constant with concentration show that the potential difference across the diffusion layer due to its resistance is

$$\eta_{r.d.} = \frac{DF}{n_- \Lambda} \ln \left(1 - \frac{i}{i_d} \right).$$

where D is the diffusion coefficient of the ion being deposited, n_- is the transport number of the other ion and i_d is the limiting current.

CHAPTER XII

XII-1.   Plot the saturation current density in amp.cm.$^{-2}$ in the range 1800° to 2400°K. for a tungsten electrode emitting electrons.

(The coefficient A in the RICHARDSON equation can be shown quantally to be equal to $\dfrac{2\pi e_0 m k^2}{h^3}$; $e_0, m,$ are the charge and mass of the electron, k is BOLTZMANN's constant and h PLANCK's constant. The electronic work function for W is 4·52 e.v.).

XII-2.   Calculate the number of positive ions formed when 1 g.mol. of caesium is heated from 1500 °K. at atmospheric pressure to 1600 °K. at a pressure of 100 cm. of mercury (electronic work function for $Cs = 3.86$ e.v.).

XII-3.   The field strength at a point between two long coaxial cylindrical electrodes, across which the p.d. is $\Delta\psi$, is given by

$$F = \frac{\Delta\psi}{r \ln \dfrac{a}{b}} \, ,$$

where b is the radius of the larger and a that of the smaller electrode, and r is the distance of the point from the axis. Show that in ZELENY's method of measuring the mobility of gas ions (Chapter XIII, p. 575) the mobility can be obtained from the expression,

$$u = \frac{Q \ln \dfrac{b}{a}}{2\pi \Delta\psi d} \, ,$$

(Q is the volume of gas passed through the tube in unit time). Hydrogen is streamed at 161 cm.^{3}sec.$^{-1}$ down a tube with the inner electrode 0·92 cm. radius and the outer electrode 8·31 cm. radius. The distance (d) between the plane in which the gas is ionised and the division of the inner electrode is 2·34 cm. The

critical potential is found to be 10·0 volts. Calculate the mobility of the ions in cm.sec.$^{-1}$volt^{-1}cm.$^{-1}$.

XII-4.   It can be shown that the velocity of diffusion (v) of ions in the x direction in the absence of an electric field is related to its diffusion coefficient D and the partial pressure of the ions P by

$$-D\frac{dP}{dx} = Pv\,.$$

Show that the mobility of the ions in an electric field is

$$u = \frac{DF}{RT}$$

where F is the Faraday. Calculate the mobility of a proton under unit potential gradient at 25 °C. if the diffusion coefficient is 1·8 cm.^{2}/sec. Suggest why this result differs from the experimental quantity of Question 3.

XII-5.   Under certain conditions 34 pairs of ions are generated per cc. per sec. in air. If the coefficient of recombination is $8400e_0$ (e_0 is the electronic charge in e.s.u.) how many positive ions will be present in a cubic centimetre of air? What will be the specific conductance of the air if the mobility of both positive and negative ions is 1·6 cm.sec.$^{-1}$volt.$^{-1}$cm.$^{-1}$?

XII-6.   Show that the velocity of an ion, of charge e, at a time t, between two parallel plates across which is a potential difference $\varDelta\psi$ is $v = \dfrac{\varDelta\psi e t}{m\,d}$, if d is the distance between the plates and the ion starts with zero velocity from the plate having a charge of the same sign as that of the ion.

Calculate the velocity of a proton on arrival at the second plate if the plate separation is 10 cm. and the potential difference across the plates is 1000 volts. How long does the proton take to cross from one plate to the other and how much energy does it deliver to the second plate?

XII-7.   If the ion in Question 6 starts from one plate with an initial

velocity (v_0) perpendicular to the plane of the plate, what is the condition that the ion will reach the opposite plate if the field is opposing its motion? An electron is released at an electrode with kinetic energy of 10^{-9} ergs travelling towards an electrode 400 v. negative with respect to the first. Which electrode will it reach and what happens to its original energy?

XII-8. An a-particle having a velocity of $2 \cdot 50 \cdot 10^7$ cm.sec.$^{-1}$ is released at an electrode and travels towards a second electrode 4 cm. from the first and 600 v. positive with respect to it. At a distance of $1 \cdot 85$ cm. from the first electrode the a particle hits a nitrogen molecule, ionises it and sends it in the same direction as the a particle was travelling, at a velocity of $1 \cdot 99 \cdot 10^6$ cm.sec. At what time does this occur? Which electrode does the a particle reach, and how long after its departure from the first electrode does this occur? (Assume that the electron ejected from the N_2 molecule has no kinetic energy. Ionisation energy of N_2 is $15 \cdot 7$ e.v.)

XII-9. It can be shown on statistical mechanical grounds that the entropy of a monatomic gas is given by

$$S = N_A k \; \ln\left(\frac{V}{N \cdot h_2} \cdot (2\,\pi\,m\,k\,T)^{'/_s}\right) + \tfrac{5}{2}$$

V is the volume of 1 g.mol., m is the mass of the atom, k is BOLTZMANN's constant, N_A AVOGADRO's number, h PLANCK's constant and T the absolute temperature.

Show that the equilibrium constant for the ionisation of a metal vapour may be written

$$\ln K_p = -\frac{Pe_0}{kT} + \tfrac{5}{2}\ln T + \tfrac{3}{2} + \ln\left(\frac{k^{'/_s}(2\,\pi\,m)^{'/_s}}{h^3}\right),$$

where P is the ionisation potential and m is the electronic mass.

XII-10. Show that the relative numbers of atoms of Cs, Rb, K, Na, Li required to give equal conductances in a flame at 2000 °C. are approximately 1, $4 \cdot 8$, $18 \cdot 2$, 1330, 5731. Assume that the ionisation potentials are Cs, $3 \cdot 87$ e.v.; Rb, $4 \cdot 15$ e.v.; K, $4 \cdot 32$ e.v.; Na, $5 \cdot 11$ e.v. and Li $5 \cdot 36$ e.v.

SOLUTIONS TO THE PROBLEMS

CHAPTER I

1-1. $n_{H^+} = 0.838.$

1-2.   Cell constant $= 3.486$ cm.$^{-1}$
$\Lambda_{BaCl_2} = 119.1$ mho.

1-3. $\varkappa_{KCl} = 7.130 \cdot 10^{-3}$ mho cm.$^{-1}$

1-4. $n_{Cl^-} = 0.6837.$

1-5.   For a DANIELL cell $E = 1.05$ v.
   (a) Since no current flows through the measuring circuit a series resistance has no effect on the balance point.
   (b) Length of wire required is 48.98 cm.

I-6. $n_{Ag^+} = 0.532.$

I-7.   The hydrogen coulometer gives a result 0.95% low in comparison with the iodine coulometer.

I-8.   Current is 0.210 amp. which is in good agreement with the value calculated from the measurements with the iodine coulometer.

I-9.   Energy due to surface tension forces $=$ (area) $\times$ (surface tension)
$$= 4 \pi r^2 \gamma$$
Energy due to potential $\quad = \frac{1}{2} C \psi^2$
$$= \frac{1}{2} \frac{q^2}{C}$$
$$= \frac{1}{2} \frac{q^2}{r}.$$

Therefore excess energy of hydrogen bubble over bulk hydrogen at the same pressure,

$$U = 4 \pi r^2 \gamma + \tfrac{1}{2} \frac{q^2}{r} \, .$$

For equilibrium $\dfrac{dU}{dr} = 0,$

and $E = 4 \sqrt{\pi r \gamma} \, .$

I-10.   From $t = 0$ to $t = t'$ the horizontal component of the force on the ion is $\dfrac{4 \pi \sigma e}{1 + m}$, if e is the ionic charge.

$\therefore$ Distance travelled is $s = \tfrac{1}{2} \cdot \dfrac{4 \pi \sigma e \, (t')^2}{(m + 1) M}$, where M is the mass of the ion.

Distance to go $= d - \dfrac{2 \pi \sigma e \, (t')^2}{(m + 1) M} \, .$

As the field is switched on the gas pressure becomes

(MAXWELL-BOLTZMANN distribution)

$$p = p_0 \, \exp. \left[- \frac{U_s}{kT} \right] \quad (p_0 = 1 \text{ atm.}),$$

where
$$U_s = - \int_{\infty}^{h} F \, e \, dh \, .$$

Hence the horizontal component of the force on the ion becomes

$$\frac{4 \pi \sigma e}{1 + m. \, \exp. \left[- \frac{U_s}{kT} \right]} \, .$$

$\therefore \quad d - \dfrac{2 \pi \sigma e \, (t')^2}{(m+1) \, M} = \dfrac{4 \pi \sigma e \, t'}{(m+1) M} (\tau - t') + \dfrac{2 \pi \sigma e \, (\tau - t')^2}{M \left(1 + m. \, \exp. \left[- \frac{U_s}{kT} \right] \right)} \, .$

Solving for the total time τ,

$$\tau = \frac{A \pm B}{C} ;$$

where
$$A = \frac{4 \pi \sigma e}{(m + 1) M} - \frac{4 \pi \sigma e \, t'}{M \left(1 + m. \, \exp. \left[- \frac{U_s}{kT} \right] \right)} \, ,$$

$$B^2 = \left[\frac{4\pi\sigma e}{(m+1)M} - \frac{4\pi\sigma e t'}{M\left(1+m.\exp.\left[-\frac{U_i}{kT}\right]\right)}\right]^2 +$$

$$\frac{8\pi\sigma e}{M\left(1+m.\exp.\left[-\frac{U_i}{kT}\right]\right)}\left[\frac{2\pi\sigma e\,(t')^2}{(m+1)M} - \frac{2\pi\sigma e\,(t')^2}{M\left(1+m.\exp.\left[-\frac{U_i}{kT}\right]\right)}\right]$$

$$C = \frac{4\pi\sigma e}{M\left(1+m.\exp.\left[-\frac{U_i}{kT}\right]\right)}.$$

CHAPTER II

II-1.   Heat required is 47·78 k.cal.

Entropy change is 55·45 cal.deg.$^{-1}$mole^{-1}.

II-2.   This graphical integration may be most readily accomplished by cutting out the graph and weighing it (although this method is approximate owing to the non-uniformity of the paper).

$S_{298} = 62\cdot39$ cal.deg.$^{-1}$mole^{-1}.

II-3.

$$dH = \left(\frac{\partial H}{\partial P}\right)_T dP + \left(\frac{\partial H}{\partial T}\right)_P dT \;;$$

$$\therefore \;\; \mu_{J.T.} = \left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\dfrac{\partial H}{\partial P}\right)_T}{C_P}.$$

$$V = T\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial H}{\partial P}\right)_T;$$

$$\mu_{J.T.} = \left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]\frac{1}{C_P}.$$

$$\left(P + \frac{a}{V^2}\right)(V-b) = RT \;;$$

$$V = \frac{RT}{P} - \frac{a}{RT} + b + \frac{ab\,P}{R^2T^2};$$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V-b}{T} + \frac{2a}{RT^2} - \frac{8abP}{R^2T^3} \ .$$

$$\therefore \ \mu_{J.T.} = \frac{1}{C_p}\left(-b + \frac{2a}{RT} - \frac{8abP}{R^2T^2}\right) .$$

$$T_i^2 - \frac{2a}{Rb}T_i + \frac{8aP}{R^2} = 0 \ .$$

$$T_i = 12 \ °K. \ or \ 2056 \ °K.$$

II-4.
$$S_B = S_A + R \ln \frac{P_A}{P_B},$$
$$or \ S = S_0 - R \ln P \ .$$

Entropy of mixing,

$$\Delta S = S_{AB} - S_A - S_B = n_A (S_{0(A)} - R \ln P_A) + n_B (S_{0(B)} - R \ln P_B)$$
$$- n_A (S_{0(A)} - R \ln P) - n_B (S_{0(B)} - R \ln P);$$

n_A, n_B = number of moles of A and B respectively and P_A, P_B are the partial pressures which are given by $P_A = N_A P$ and $P_B = N_B P$, where N_A, N_B are mole fractions.

$$\therefore \quad \Delta S = -n_A R \ln N_A - n_B R \ln N_B ,$$

which is the entropy change for $n_A + n_B$ moles.

For one mole $\Delta S = -R (N_A \ln N_A + N_B \ln N_B) ,$
or in general $\Delta S = -R \sum_i N_i \ln N_i .$

II-5. Red PbO,
$$\Delta G = -58,221 + 0.07 \ T \ln T - 0.488 . 10^{-3} . T^2 + 85.64 . T^{\frac{1}{2}}$$
$$+ 21.57 \ T.$$

Yellow PbO,
$$\Delta G = -52,821 + 0.07 \ T \ln T - 0.488 . 10^{-3} . T^2 + 85.64 . T^{\frac{1}{2}}$$
$$+ 20.56 \ T.$$

For the transition from the yellow to the red modification
$$\Delta G = -400 + 1.01 \ T .$$

The transition temperature is thus $396 °K.$

The red oxide is stable at room temperature.

II-6. C—H — 87.25 k.cal.
C—C — 55.54 k.cal.
C=C — 98.84 k.cal.
Heat of formation of benzene from bond energies = 971.6 k.cal,

and from combustion data $= 1004 \cdot 5$ k.cal. The difference of 88 k.cal. is due to the stabilisation of the molecule by resonance.

II-7.   The most satisfactory method is to plot kilogram molality against volume containing $1000\,g.$ of solvent. The slope of the curve then gives the partial molar volume of the solute.

m	V_s
$0 \cdot 2$ m	30 cc.
1 m	
8 m	} 50 cc.
5 m	

II-8.   This is the GIBBS adsorption equation. For derivation see *e.g.*, ADAM, *The Physics and Chemistry of Surfaces*, Oxford, 1944, Chapter III.

II-9.
$$C_P = \left(\frac{\partial q}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial S}{\partial V}\right)_P\left(\frac{\partial V}{\partial T}\right)_P .$$

According to MAXWELL's equations,

$$\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S , \text{ and } \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T ,$$

$$\therefore\ C_P = -\frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_S\left(\frac{\partial S}{\partial P}\right)_T .$$

Similarly
$$C_V = \frac{1}{T}\left(\frac{\partial S}{\partial P}\right)_V\left(\frac{\partial P}{\partial T}\right)_V .$$

MAXWELL's equations,

$$\left(\frac{\partial P}{\partial S}\right)_V = -\left(\frac{\partial T}{\partial V}\right)_S , \text{ and } \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T .$$

$$\therefore\ C_V = -\frac{1}{T}\left(\frac{\partial V}{\partial T}\right)_S \cdot \left(\frac{\partial S}{\partial V}\right)_T .$$

$$\therefore\ \frac{C_P}{C_V} = \frac{\left(\dfrac{\partial P}{\partial T}\right)_S\left(\dfrac{\partial S}{\partial P}\right)_T}{\left(\dfrac{\partial V}{\partial T}\right)_S\left(\dfrac{\partial S}{\partial V}\right)_T} = \frac{\left(\dfrac{\partial P}{\partial V}\right)_S}{\left(\dfrac{\partial P}{\partial V}\right)_T} .$$

II–10.　The thermopile may be considered as a CARNOT reversible engine. Thus $\dfrac{0.1}{293.1}$ of the incoming radiation ($5.2 \cdot 10^8$ erg/sec.) is converted into useful work.

The maximum power available is $1.78 \cdot 10^{-4}$ watts.

CHAPTER III

III–1.　CsF,　$U_0 = -171.1$ k.cal
　　　CsCl,　$U_0 = -146.3$ k.cal
　　　CsBr,　$U_0 = -141$　　k.cal
　　　CsI,　　$U_0 = -134$　　k.cal

III–2.　CsF,　　$U = -173.6$ k.cal
　　　CsCl,　　$U = -151.5$ k.cal
　　　CsBr,　　$U = -145.8$ k.cal
　　　CsI,　　　$U = -138.6$ k.cal

III–3.　CsF　$Q_+ + Q_- = -179.9$ k.cal.
　　　CsCl　$Q_+ + Q_- = -141.6$ k.cal.
　　　CsBr　$Q_+ + Q_- = -134.3$ k.cal.
　　　CsI　　$Q_+ + Q_- = -125.6$ k.cal.
For Cs,　　　$Q_+ = -93.8$ k.cal., which can be combined with the values for anions given in the text to compare with the solvation energies evaluated above.

III–4.　The percentage error is given by $\dfrac{100\,l^2}{4r^2}\cos^2\varphi$, or 0.97%.

$$\varphi = \ \ 0°, \qquad r = 2.5 \text{ Å}.$$
$$\varphi = 45°, \qquad r = 1.75 \text{ Å}.$$
$$\varphi = 60°, \qquad r = 1.25 \text{ Å}.$$
$$\varphi = 90°, \qquad r = 0.$$

III–5.　Following the method used in the text, (p. 106)

$$U = \frac{2\,e\,e_0}{r} - \frac{e\,e_0}{r + l\cos\varphi} - \frac{e\,e_0}{r - l\cos\varphi};$$

$$= -\frac{2\,e\,e_0\,l^2\cos^2\varphi}{r(r^2 - l^2\cos^2\varphi)}.$$

Approximately

$$U = -\frac{2\,e\,e_0\,l^2\cos^2\varphi}{r^3}.$$

$$r_{\text{HCl}} = 0.55\,(r_{\text{CO}_2})^{1/2}.$$

III-6.   The potential at a point due to a dipole is,

$$\psi : \quad \frac{\mu\cos\theta}{r^2}$$

The field at this point may be found as the resultant of the field along the r direction and the direction perpendicular to it.

Along r, $F_1 = -\dfrac{\partial\psi}{\partial r} = -\dfrac{\partial}{\partial r}\left(\dfrac{\mu\cos\theta}{r^2}\right),$

$$= \frac{2\,\mu\cos\theta}{r^3}.$$

Perpendicular to r, $F_2 = -\dfrac{1}{r}\dfrac{\partial\psi}{\partial\theta},$

$$= \frac{\mu\sin\theta}{r^3}.$$

Resultant field,

$$R = \sqrt{\left(\frac{2\,\mu\cos\theta}{r^3}\right)^2 + \left(\frac{\mu\sin\theta}{r^3}\right)^2}$$

$$= \frac{\mu}{r^3}\sqrt{3\cos^2\theta + 1}.$$

Field inducing dipole 2 due to dipole 1,

$$\mathcal{F}_{1\to2} = \frac{\mu_1}{r^3}\sqrt{3\cos^2\theta_1 + 1};$$

and energy $U_{1\to2} = -\tfrac{1}{2}\,a_2\left(\dfrac{\mu_1}{r^3}\sqrt{3\cos^2\theta_1+1}\right)^2.$

Similarly for energy of dipole 2 interacting with induced dipole 1

$\therefore$ Total energy of interaction,

$$U = U_{1\to2} + U_{2\to1}$$

$$= -\frac{1}{2r^6}\left\{a_2\mu_1^2(3\cos^2\theta_1 + 1) + a_1\mu_2^2(3\cos^2\theta_2 + 1)\right\}.$$

Averaging over all directions for random rotation μ_1^2 and μ_2^2

become the mean values $\bar{\mu}_1{}^2$ and $\bar{\mu}_2{}^2$, and the average value of $\cos^2 \theta$ over all angles in space is $\frac{1}{3}$.

Thus, $$U = -\frac{a_2 \bar{\mu}_1{}^2}{r^6} - \frac{a_1 \bar{\mu}_2{}^2}{r^6};$$

or if the dipoles are identical

$$U = -\frac{2a\bar{\mu}^2}{r^6}.$$

III-7. The interaction energy between two non polar atoms may be considered to be due to the induced dipole moments when the atoms are close together. (The polarisability can be put approximately equal to $r_0{}^3$ if r_0 is the atomic radius, c/. RICE, *Electronic Structure and Chemical Binding*, McGRAW HILL, 1940.)

The dipole may very approximately be assumed to be due to the outermost electron and the resultant positive charge of the nucleus together with the remaining electrons. Its moment will thus be approximately $e\, r_0$.

$$\therefore\ U = -\frac{2 a e^2 r_0{}^2}{r^6}.$$

The energy of the outermost electron is $-\dfrac{e^2}{2r_0}$, approximately, if the atom is hydrogen-like, and this is the energy $-I$, where I is the ionisation energy.

$$U = -\frac{4 a r_0{}^3 I}{r^6};$$

$$4 a^2 I$$

This is of course a very rough formula and gives only an order result.

For neon $\qquad\qquad U = 0 \cdot 52$ k.cal.

The experimental value corrected to $0\,°K.$ is $0 \cdot 59$ k.cal.

III-8. For a monatomic gas the SACKUR TETRODE equation is

$$S = 4 \cdot 576 \left(\tfrac{3}{2} \log_{10} M + \tfrac{5}{2} \log_{10} T - \log_{10} P - 0 \cdot 5055 \right).$$

M is the molecular weight in atomic weight units,

T the absolute temperature,

P the pressure in atmospheres.

Entropy of gas ions at 25 °C. at concentration 1 mol/litre.

H^+	19·7 cal.deg.$^{-1}$g.ion^{-1}.
Na^+	29·0
Rb^+	32·9
F^-	28·5
Cl^-	30·3
I^-	34·1

Entropy defect = experimental entropy — calculated without allowance for solvation.

H^+	23·3 cal.deg.$^{-1}$g.ion^{-1}.
Na^+	19·6
Rb^+	13·5
F^-	30·9
Cl^-	12·0
I^-	4·0

Entropy change during solidification of 1 mol water at 25 °C. is —6·05 cal.deg.$^{-1}$.

Hence, solvation numbers are

H^+	3·8
Na^+	3·2
Rb^+	2·2
F^-	5·1
Cl^-	2·0
I^-	0·6

III-9.   If a is the incompressible fraction of the solvent

$$\beta = \beta_0 (1 - a), \quad \therefore \quad a = 1 - \frac{\beta}{\beta_0} .$$

In a solution of g grams solute in 100 grams solution there are $100 - g$ grams solvent.

$\therefore$ amount of the solvent in 100 g. solution which is incompressible is $\left(1 - \dfrac{\beta}{\beta_0}\right)(100 - g)$.

Amount of incompressible water per gram of solute is

$$h = \frac{\left(1 - \dfrac{V_0^2 \varrho_0}{V^2 \varrho}\right)(100 - g)}{g} \; .$$

	g	h	Solvation number at infinite dilution	S_0
NaCl	1·0	2·36	7·66	
	5·31	2·07	6·74	Approx. 8
	21·25	1·38	1·38	
NaI	1·32	0·821	6·79	
	8·19	0·729	6·52	Approx. 7
	13·78	0·687	5·68	

III–10.

$$\text{Radius of ion} = \frac{e_0}{300}\left[\frac{1 - \dfrac{e_0^2 \varkappa}{6\,DkT(1 + \sqrt{0\cdot5})}}{6\,\pi\,u_i\,\eta + \dfrac{e_0 \varkappa}{300}}\right] \; .$$

c	Radius of ion	Vol. of water attached to 1 g.ion	Solvation number
0	2·36 . 10^{-8} cm.	32·6 cc.	8·6
0·01	2·34 . 10^{-8} cm.	31·8 cc.	8·5
0·02	2·31 . 10^{-8} cm.	31·0 cc.	8·4
0·03	2·23 . 10^{-8} cm.	27·0 cc.	8·0
0·10	2·18 . 10^{-8} cm.	23·8 cc.	2·6

CHAPTER IV

IV–1.　　0·01M, $a = 0·915$.
　　　　0·05M, $a = 0·688$.

IV–2.

	$c \cdot 10^4$	$K \cdot 10^4$	
MeOH:	0·9662	6·3	
	1·8148	6·4	
	3·0758	6·7	Mean $K = 6·6 \cdot 10^{-4}$.
	4·7296	6·75	
	6·5885	6·85	
	9·1630	7·0	

		$K \cdot 10^5$	
EtOH:	1·0388	9·35	
	2·2022	10·1	
	3·8952	10·4	Mean $K = 1·05 \cdot 10^{-4}$.
	6·0849	10·8	
	8·5763	11·1	
	11·4924	11·3	

IV–3.   Mean value, $K = 5·02 \cdot 10^{-4}$.

IV–4.

c	f_0
2·0	0·684
5·0	0·748
10·0	0·862
15·0	0·948
22·50	1·087.

IV–5.   From the given equation,

$$\log_{10} F = \log_{10} P - 5·887 \cdot 10^{-5} P - 5·598 \cdot 10^{-9} P^2 .$$

Hence, activity of solvent, $a_1 = F/F_0$.

P	F	a_1
285·8	228·2	0·3391
373·8	354·7	0·5270
489·1	456·8	0·6779
648·8	586·8	0·8719
692·0	626·1	0·9808
718·6	648·5	0·9562
726·5	658·5	0·9715

P	F	a_1
788·4	659·4	0·9797
786·6	661·9	0·9835
789·2	664·0	0·9866
742·0	666·2	0·9899
744·0	667·8	0·9923
745·1	668·7	0·9936
750·6	673·0	1·000

IV-6.

m_{NaCl}	I	$f_{(m)}$
0·	0·02248	0·866
0·1024	0·1280	0·760
0·2025	0·2297	0·715
0·6096	0·6400	0·640
1·0289	1·061	0·608
1·5394	1·572	0·589

$m_0 = 0\cdot01945.$

m_{LiNO_3}	I	$f_{(m)}$
0·03075	0·05472	0·809
0·09232	0·1180	0·754
0·2039	0·2320	0·689
0·4112	0·4417	0·636
0·8179	0·8514	0·578

$m_0 = 0\cdot01938.$

IV-7.

$c_{K_2SO_4}$	I	$f_{(c)}$
0	0·000464	0·951
0·0006	0·001384	0·909
0·0010	0·001992	0·895
0·0020	0·003515	0·854
0·0030	0·005033	0·826
0·0050	0·008063	0·781

$c_{K_3Co(CN)_6}$	I	$f_{(c)}$
0·0010	0·002490	0·889
0·0020	0·004158	0·849
0·0050	0·010570	0·777

IV-8.   Variation of activity of a solid close to its melting point is given by

$$\frac{d\ln a_s}{dT} = -\frac{\Delta H_s}{RT_s} .$$

Also,

$$\Delta H_s = \Delta H_\theta - \Delta C_p \, \Delta T ,$$

where ΔH_θ is the heat of solidification at the melting point, ΔT is the difference of the temperature from the melting point, and ΔC_p is the difference of the heat capacities of the solid and liquid state.

$$\therefore \quad d\ln a_s = \frac{d(\Delta T)}{RT_\theta^2} \; \Delta H_\theta + \left[\frac{2\Delta H_\theta}{T_0} - \Delta C_p \right] \Delta T + \ldots$$

For water $d(\ln a_s) = (-0.009696 - 1.03 . 10^{-5} \, \Delta T) \, d(\Delta T)$.

At the freezing point the activity of the solid solvent is equal to that of the liquid solvent (a_1) ;

and

$$d\ln a_2 = -\frac{N_1}{N_2} d\ln a_1 .$$

$$\therefore \quad d\ln a_2 = \frac{d(\Delta T)}{1.858 m_2} + 0.00057 \frac{\Delta T \, d(\Delta T)}{m_2} ;$$

or for an electrolyte,

$$d\ln a_2 = \frac{d(\Delta T)}{1.858 \nu m_2} + 0.00057 \frac{\Delta T \, d(\Delta T)}{\nu m_2} .$$

Introducing j this equation becomes,

$$d\ln \frac{a_2}{m_2} = -j \, d\ln m_2 - d \, j + 0.00057 \frac{\Delta T}{\nu m_2} d(\Delta T) ,$$

which is the differential form of the required equation.

m_2	a_2/m_2
0.1	0.802
0.5	0.665
1.0	0.610
1.5	0.579

These results differ slightly from those given by JONES and BURY who integrated by the alternative method of RANDALL (*J. Am. Chem. Soc.*, 1926, **48**, 2512).

IV-9.   Under conditions of equal vapour pressure the solvent activities (a_s) is the same in both solutions.

$$d\ln a_s = \frac{m_1}{m_s} d\ln a_1 = \frac{m_2}{m_s} d\ln a_2 .$$

$$dm_1 + m_1 \, d\ln f_{(m)_1} = dm_2 + m_2 \, d\ln f_{(m)_2} .$$

$$\frac{dm_1}{m_2} + \frac{m_1}{m_2} d\ln f_{(m)_1} = d\ln m_2 + d\ln f_{(m)_2} .$$

$$d\ln f_{(m)_2} = d\ln f_{(m)_1} + d\ln \frac{m_1}{m_2} + \left(\frac{m_1}{m_2} - 1\right) d\ln f_{(m)_1} m_1 ,$$

or $$\ln f_{(m)_2} = \ln f_{(m)_1} + \ln \frac{m_1}{m_2} + 2 \int_0^{\sqrt{a_1}} \left(\frac{m_2}{m_1} - 1\right) \frac{d\sqrt{a_1}}{\sqrt{a_1}} .$$

m	$f_{(m)_{LiI}}$
0·1	0·811
0·2	0·794
0·3	0·795
0·5	0·806
0·7	0·835
1·0	0·903
1·5	1·019
2·0	1·190
2·5	1·394

IV-10.   Ideal osmotic pressure, $\Delta\pi_{ideal} = \nu n RT$.

Real osmotic pressure, $\Delta\pi = f_0 \nu n RT$.

$$\therefore \quad \frac{\Delta\pi_{ideal} - \Delta\pi}{\Delta\pi} = 1 - f_0 .$$

The VAN 'T HOFF factor, $i = 1 + (\nu - 1) a = \nu f_0$.

$$\therefore \quad 1 - f_0 = \frac{\nu - 1}{\nu} (1 - a) .$$

Introducing OSTWALD's dilution Law,

$$1 - f_0 = \frac{(\nu - 1) m^{\nu-1} a^\nu}{\nu K} .$$

For dilute solution, $a^\nu = 1$.

The curve of $1 - f_0$ plotted against νm should approach the origin as a tangent to the νm axis.

Classically, solutions having the same value of νm should be isotonic since it is assumed that the valency of the ions does not affect their osmotic behaviour. The experimental evidence that the νm against $1 - f_0$ lines differ for different valence types throws doubt on this assumption.

CHAPTER V

V-1. 20% Dioxan:

		15 °C.	45 °C.
	$0.1M$	2.19 Å	2.13 Å
	$0.01M$	6.93	6.74
	$0.001M$	21.9	21.3
	$0.0001M$	69.3	67.4

82% Dioxan:

	$0.1M$	0.866 Å	0.845 Å
	$0.01M$	2.74	2.67
	$0.001M$	8.66	8.45
	$0.0001M$	27.4	26.7

V-2. $f_{\pm}^{\nu} = f_+^{\nu_+} \cdot f_-^{\nu_-}$.

$\log f_{\pm} = - z_+ z_- \, A \sqrt{I}$.

$\log f_- = - z_-^2 \, A \sqrt{I}$.

$\nu \log f_{\pm} = \nu_+ \log f_+ + \nu_- \log f_-$.

$\log f_+ = \dfrac{\nu}{\nu_+} \log f_{\pm} - \dfrac{\nu_-}{\nu_+} \log f_-$.

$\log f_- = \dfrac{z_-}{z_+} \log f_{\pm}$.

$\log f_+ = \dfrac{\nu}{\nu_+} \log f_{\pm} - \dfrac{z_-}{z_+} \dfrac{\nu_-}{\nu_+} \log f_{\pm}$.

$\quad\;\; = \left(\dfrac{\nu}{\nu_+} - 1 \right) \log f_{\pm}$.

Similarly for $\log f_-$.

V-3.

$\sqrt{I}$	f_1
0·0872	0·918
0·0447	0·902
0·0593	0·872
0·0709	0·849
0·0897	0·813

$$\log f_1 = -1{\cdot}000 \sqrt{I}$$

V-4. Consider the ions to be charged slowly so that at any given time their charge is λ of the final charge. The potential at any given time is then λ^2 of the final potential, because $\psi_i = -\dfrac{e_i \varkappa}{\varepsilon}$, and $\varkappa$ is proportional to e_i ($e_i = z_i e_0$).

The work done during a time element is,

$$(\lambda^2 \psi_i)\,(e_i\, d\lambda)\,.$$

$\therefore$ Total work in charging $= \sum_i N_i \displaystyle\int_0^1 \lambda^2 \psi_i e_i\, d\lambda$,

$$= \sum_i \frac{N_i e_i \psi_i}{3} \qquad \sum_1 \frac{N_i e_i^2 \varkappa}{3\,\varepsilon}$$

The work, $-\sum_j \dfrac{N_i e_i^2 \varkappa}{2\varepsilon}$ (equation 20), is the work done in removing the charge from the ions, keeping them fixed in their original configuration; then restoring the charge at infinite dilution.

$-\sum_j \dfrac{N_i e_i^2 \varkappa}{3\,\varepsilon}$ is the work required when the ions have a distribution corresponding to the amount of charge at any given instant. Thus, the energy required is smaller because at each readjustment of the distribution the thermal motion does work against the interionic forces.

V-5. $\Delta\pi_{\text{obs.}} = \Delta\pi_0. - \Delta\pi_{\text{el.}}$, and $f_0 = \dfrac{\Delta\pi_{\text{obs.}}}{\Delta\pi_0.}$

$\Delta\pi_{\text{obs.}}$, observed osmotic pressure.

$\Delta\pi_0.$, ideal osmotic pressure.

$\Delta\pi_{\text{el.}}$, change in osmotic pressure due to interionic effects.

$$\therefore \quad 1 - f_0 = \frac{\Delta \pi_{\text{el.}}}{\Delta \pi_0.}\;.$$

$$\Delta \pi_{\text{el.}} = \left(\frac{\partial \mu_{\text{el.}}}{\partial V}\right)_T = \left\{\frac{\partial}{\partial V}\left(\frac{-\Sigma N_i (z_i e_0)^2 \varkappa}{3 \varepsilon}\right)\right\}_T,$$

$$= + \frac{\Sigma N_i (z_i e_0)^2 \varkappa}{6 \varepsilon V}\;.$$

$$\Delta \pi_0. = \Sigma N_i \frac{kT}{V};$$

$$\therefore \quad 1 - f_0 = \frac{\Sigma N_i (z_i e_0)^2 \varkappa}{6 \varepsilon \Sigma N_i kT}\;,$$

$$= \frac{e_0^2 \Sigma N_i z_i^2}{6 \varepsilon kT \Sigma N_i}\left(\frac{4 \pi e_0^2 \Sigma N_i z_i^2}{\varepsilon kT}\right)^{1/2},$$

$$= \frac{e_0^3 \pi^{1/2} \Sigma N_i z_i^2}{8 (\varepsilon kT)^{1/2} \Sigma N_i} (\Sigma N_i z_i^2)^{1/2}\;.$$

V–6.
$$-\frac{\Delta H}{T^2} = \left[\frac{\partial\left(\dfrac{\mu_{\text{el.}}}{T}\right)}{\partial T}\right]_P.$$

$$\Delta H = -T^2 \frac{\partial}{\partial T}\left(-\frac{\Sigma N_i z_i^2 e_0^2 \varkappa}{3 \varepsilon T}\right),$$

$$= -\frac{\Sigma N_i z_i^2 e_0^2 \varkappa}{2 \varepsilon}\left[1 + \frac{T}{\varepsilon}\frac{\partial \varepsilon}{\partial T} + \frac{T}{3V}\frac{\partial V}{\partial T}\right],$$

$$= -D_c\;.$$

V–7.
$$S_{\text{el.}} = -\left(\frac{\partial \mu_{\text{el.}}}{\partial T}\right)_P = \frac{\partial}{\partial T}\left(-\frac{\Sigma N_i z_i^2 e_0^2 \varkappa}{3 \varepsilon}\right),$$

$$= + \frac{\Sigma N_i z_i^2 e_0^2}{8}\sqrt{\frac{4 \pi e_0^2 \Sigma N_i z_i^2}{k}}\frac{\partial}{\partial T}(\varepsilon^{-1/2} T^{-1/2} V^{-1/2})\;.$$

Putting the constant terms equal to A;

$$S_{\text{el.}} = + A\left[-\tfrac{1}{2}\varepsilon^{-1/2}T^{-3/2}V^{-1/2}\frac{\partial V}{\partial T} - \tfrac{1}{2}\varepsilon^{-1/2}V^{-1/2}T^{-3/2}\right.$$
$$\left. - \tfrac{1}{2}V^{-1/2}T^{-1/2}\varepsilon^{-1/2}\frac{\partial \varepsilon}{\partial T}\right].$$

$$(C_p)_{\text{el.}} = \frac{1}{T}\left(\frac{\partial S_{\text{el.}}}{\partial T}\right)_P,$$

$$= +\frac{\Sigma N_i z_i^2 e_0^2 \varkappa}{4\,\varepsilon\,T}\left[1 + \frac{2\,T}{3}\frac{\partial V}{V\,\partial T} + \frac{2\,T}{\varepsilon}\frac{\partial \varepsilon}{\partial T} + \left(\frac{T}{V}\frac{\partial V}{\partial T}\right)^2 + \right.$$

$$\left.\left(\frac{T}{\varepsilon}\frac{\partial \varepsilon}{\partial T}\right)^2 + \frac{2\,T^2}{\varepsilon V}\frac{\partial V}{\partial T}\frac{\partial \varepsilon}{\partial T} - \frac{2}{3}\frac{T^2}{V}\frac{\partial^2 V}{\partial T^2} - \frac{2\,T^2}{\varepsilon}\frac{\partial^2 \varepsilon}{\partial T^2}\right].$$

$$C_p = (C_p)_0. - (C_p)_{\text{el.}}.$$

V-8.   The approximate condition may be found by solving $\dfrac{z e_0\,\bar\psi}{kT} = 1$,

and $\bar\psi = \dfrac{z e_0}{\varepsilon}\dfrac{e^{-\varkappa r}}{r}$ graphically.

> 1—1 electrolyte, $r_{\text{crit.}} = 6\cdot 7$ Å.
> 3—1 electrolyte, $r_{\text{crit.}} = 30$ Å.

V-9.   Mean value of C is 0·048.

For a non-electrolyte z_1 and $z_2 = 0$, and the HÜCKEL equation becomes,

$$\log f_u = C I,$$
$$\text{or}\qquad \log f_u = C c,$$

in a solution of a 1 : 1 electrolyte.

SETSCHENOV's equation for salting out is,

$$\log \frac{s_0}{s} = k c.$$

The non-electrolyte in solution is in equilibrium with solid non-electrolyte, thus, its chemical potential is independent of the presence of an electrolyte.

Hence, $a_0 = a$,

or $s_0 f_{u,0} = s f_u$.

The activity coefficient of the non-electrolyte in a saturated solution in the absence of an electrolyte is close to unity.

$$\therefore \log \frac{s_0}{s} = \log f_u = C c.$$

At constant temperature and pressure the absorption coefficient

of a gas is directly proportional to its solubility, using the above equation the absorption coefficient of nitrogen in $2m$-NaCl is found to be 0·0114.

V–10.   Potential $\psi_r = \dfrac{z_i e_0}{\varepsilon r}\left[\dfrac{e^{\varkappa a}}{1+\varkappa a}\,e^{-\varkappa r}\right]$,

$\therefore$ Field $= -\dfrac{\partial \psi_r}{\partial r} = \dfrac{z_i e_0}{\varepsilon r^3}\left[\dfrac{e^{\varkappa a}\,e^{-\varkappa r}(\varkappa r+1)}{1+\varkappa a}\right]$.

Energy of dipole of permanent moment μ and polarisability a in field F is $\frac{1}{2}\,a\,F^2 + \mu\,F\cos\theta$

$\therefore\ N_r = N_0\exp.\left[(a_A - a_B)\dfrac{F^2}{2} + (\mu_A\cos\theta_A - \mu_B\cos\theta_B)F\right]\dfrac{1}{kT}$

From which the required expression can be obtained by substituting for F.

CHAPTER VI

VI–1.   NaAsO$_2$, $K_h = 1\cdot 20 \cdot 10^{-5}$.

KAsO$_2$, $K_h = 9\cdot 3 \cdot 10^{-6}$.

VI–2.

ml NaOH added	$\varkappa \cdot 10^3$
0	4·10
0·01	4·07
0·10	8·81
0·50	2·64
0·80	1·76
1·00	1·17
1·20	1·52
1·50	2·18

VI–3.

T °C.	Solubility (mol/l) 10^6
18	9·85
25	10·4
50	14·05
100	16·1

VI-4.   By plotting log [acetic anhydride] against time the reaction is found to be of the first order.

$$k_1 = 8 \cdot 47 \cdot 10^{-4} \text{ sec.}^{-1} .$$

VI-5.
$$K = \frac{a^2 f^2 c}{1-a} .$$

Mean K

Methanol: $\log_{10} f = -2 \cdot 11 \sqrt{c_i};$ $5 \cdot 40 \cdot 10^{-4} .$
Ethanol: $\log_{10} f = -2 \cdot 82 \sqrt{c_i};$ $0 \cdot 79 \cdot 10^{-4} .$

VI-6.   The energies of activation may be obtained from the slopes of the plots of log $\varkappa$ against $1/T$, and log $1/\eta$ against $1/T$.
$$E_\varkappa = 8 \cdot 2 \text{ k.cal.}$$
$$E_\eta = 4 \cdot 4 \text{ k.cal.}$$

WALDEN's rule may be tested by plotting the values of log Λ against those of log $1/\eta$ obtained at the same temperature. The required equation is $\Lambda^{1 \cdot 15} \eta = 1 \cdot 69 .$

VI-7.   According to STOKES's law the velocity (u) of a spherical particle (radius R) travelling in a viscous medium (viscosity η) under a force (P) is

$$u = \frac{P}{6\pi\eta R} .$$

Or since the mobility of an ion is proportional to its velocity under unit field,

$$l_\infty = \frac{K}{R} .$$

For a non-spherical substance R may be called the radius of the equivalent sphere, and the volume of the equivalent sphere may be written $V = K' n^{x'}$, where n is the number of unit volume elements and x' is a constant index.

Then $R = k' n^{\overline{3}};$

or $l_\infty = \frac{k''}{n^x};$

or $\log l_\infty = \text{const.} - x \log n$

The value of x may be obtained by a method of successive approximations, assuming a suitable value for the number of volume equivalents in a —COO' group, and plotting $\log l_\infty$ against $\log n$ to obtain a better value.

$$\log l_\infty = 1\cdot 915 - 0\cdot 273 \log n .$$

$$n_{-\text{COO}'} = 1\cdot 37 .$$

$$\text{For } C_{18}H_{36}(\text{COO}')_2, \quad l_\infty = 88\cdot 2 .$$

VI-8. The observed mobility of sodium will be given by,

$$(l_{\text{Na}})_{\text{obs.}} = f (l_{\text{Na}})_{\text{free}} - (1 - f) l_A .$$

The conductance of the solution is given by,

$$\Lambda = (l_{\text{Na}})_{\text{obs.}} + l_A ;$$
$$= f [(l_{\text{Na}})_{\text{free}} + l_A] .$$

c	f_{NaCl}	$f_{\text{Na}_2\text{SO}_4}$
0·0891	0·68	0·74
0·02970	0·73	0·77
0·01367	0·89	0·82

VI-9. Using, $\quad \Lambda_v = \Lambda_\infty - (C'\Lambda_\infty + C'')\sqrt{a\,c} .$
$$C' = 4\cdot 876, \quad C'' = 190\cdot 3 .$$

By the method of successive approximations,

$$c = \ 2\cdot 547 . 10^{-4} \quad K = \ 1\cdot 42 . 10^{-4} .$$
$$c = 0\cdot 2287 . 10^{-4} \quad K = 0\cdot 992 . 10^{-4} .$$

VI-10. *cf.* MEAD, FUOSS and KRAUSS, (*Trans. Faraday Soc.*, 1936, **32**, 594).

$$\Lambda_v = a (\Lambda_\infty - A \sqrt{a\,c}) . \tag{1}$$

$$\therefore \quad a = \frac{\Lambda_v}{\Lambda_\infty - A\sqrt{a\,c}} , \tag{2}$$

$$= \frac{\Lambda_v}{\Lambda_\infty - A \left[\dfrac{c\,\Lambda_v}{\Lambda_\infty - A\sqrt{a\,c}}\right]^{\frac12}} ,$$

$$= \frac{\Lambda_v}{\Lambda_\infty} \cdot \frac{1}{1 - \dfrac{A (\Lambda_v\,c)^{\frac12}}{\Lambda_\infty} \left[\dfrac{1}{\Lambda_\infty - A \sqrt{a\,c}}\right]^{\frac12}} ; \tag{3}$$

and continuing to substitute for a in equation (8) by the value from equation (2),

$$a = \frac{\Lambda_v}{\Lambda_\infty}\left[1 - z\left[1 - z\left\{1 - z(1 - z \dots)^{-\frac{1}{2}}\right\}^{-\frac{1}{2}}\right]^{-\frac{1}{2}}\right]^{-1},$$

if $\dfrac{A(\Lambda_v c)^{\frac{1}{2}}}{\Lambda_\infty^{\prime/_2}}$ is put equal to z;

or $a = \dfrac{\Lambda_v}{\Lambda_\infty F_{(z)}}$.

$$K = \frac{a^2 f^2 c}{1 - a},$$

$\therefore$ $1 = \dfrac{c f^2 a^2}{K} + a ,$

$$= \frac{c f^2}{K}\left(\frac{\Lambda_v}{\Lambda_\infty F_{(z)}}\right)^2 + \frac{\Lambda_v}{\Lambda_\infty F_{(z)}} .$$

$$\frac{F_z}{\Lambda_v} = \frac{c f^2}{K} \cdot \frac{\Lambda_v}{\Lambda_\infty^2 F_{(z)}} + \frac{1}{\Lambda_\infty} .$$

Both K and Λ_∞ may then be obtained by plotting $\dfrac{F_{(z)}}{\Lambda_v}$

against $\dfrac{c \Lambda_v f^2}{F_{(z)}}$, when a straight line should be obtained with

slope $\dfrac{1}{K(\Lambda_\infty)^2}$, and intercept on the $\dfrac{F_{(z)}}{\Lambda_v}$ axis of $\dfrac{1}{\Lambda_\infty}$,

$c \cdot 10^4$	z	$F_{(z)}$
2·547	0·0841	0·9122
1·172	0·0639	0·9337
0·4866	0·0454	0·9548
0·2287	0·0332	0·9667

$$K = 0{\cdot}80 \cdot 10^{-4} .$$

CHAPTER VII

VII-1. $\frac{1}{2} Hg_2Cl_2 + Tl \rightleftarrows TlCl + Hg$.
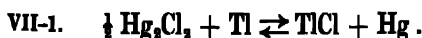
$$\Delta H = -11{,}650 \text{ cal.mole}^{-1}.$$

$$\Delta S = \quad 17 \cdot 29 \text{ cal.deg.}^{-1}\text{mole}^{-1}.$$

(a) $5{,}150 \text{ cal.mole}^{-1}.$

(b) —$11{,}650 \text{ cal.mole}^{-1}.$

Since $\Delta S = F \left(\dfrac{\partial E}{\partial T}\right)_P$, and ΔS varies with temperature in general; $\left(\dfrac{\partial E}{\partial T}\right)_P$ would vary with temperature.

VII-2.

c_1	n_{K^+}
0·05	0·498
0·1	0·496
0·5	0·494
1	0·496 .

These are mean transport numbers over the concentration range in each cell. The simple procedure of calculating n_+ may be used because the transport numbers in these cells vary very little with concentration.

VII-3.   The e.m.f. of the standard Li electrode against the normal calomel electrode is —$3\cdot8044$ v.

Differential heat of solution $= -19{,}680 \text{ cal.mole}^{-1}$.

VII-4.

	H_2SO_4	HCl
N	12·1 mv.	13·3 mv.
$N/10$	4·0	4·3
$N/100$	2·6	2·7.

It is thus only with dilute solutions that the liquid junction potential becomes reduced to a small quantity by means of a saturated KCl bridge.

VII-5.

	550°	600°
N_{KCl}	$f_{(D)}$	$f_{(D)}$
0	1	1
0·05	0·914	0·872
0·10	0·837	0·854
0·20	0·818	(0·947)
0·30	0·523	0·612
0·40	0·259	0·333

VII-6. $E_{0(Ba)} = -2 \cdot 904$ v.

$$Hg \mid Hg_2SO_4 \mid BaSO_4 \mid Ba^{++} .$$
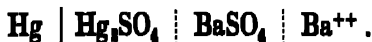
$$E = 0 \cdot 909 + \frac{RT}{2F} \ln a_{Ba^{++}} \text{ v.}$$

VII-7. The true E_0 may be obtained by first calculating rough values of E_0 for each concentration, then extrapolating to $m_{Hg} = 0$ to eliminate the liquid junction potential, and finally, extrapolating the second approximation E_0 values to zero acid concentration.

$$E_0 = 0 \cdot 9050 \text{ v.}$$

VII-8. $$E = E_0 - \frac{RT}{n_aF} \ln a_1^{v_1} a_2^{v_2}$$

$$E + 0 \cdot 088731 \, (0 \cdot 20069 + \log m) = E_0 - 0 \cdot 088731 \log f_{(m)} ,$$
$$= E'$$

Hence plotting E' against $\sqrt{m}$, and extrapolating

$$E_0 = 0 \cdot 84820 \text{ v.}$$

m_1	$f_{(m)}$
0·01729	0·444
0·01647	0·468
0·01235	0·508
0·01097	0·516
0·008227	0·552
0·004112	0·642
0·002056	0·721
0·001028	0·794

VII-9. $E_{0 N_2} = -3 \cdot 80$ v., at 1 atm.
  (a) $E = 3 \cdot 47$ v, at 1 mm. of Hg.
  (b) $E = 3 \cdot 18$ v,. at 100 atm.

VII-10. $E_{0 (Mg)} = -2 \cdot 375$ v.

CHAPTER VIII

VIII-1.   Ag $\Big|$ $\begin{array}{c}\text{AgNO}_3\\\downarrow\text{ KBr}\end{array}$ $\Big|$ NH$_4$NO$_3$ $\Big|$ reference electrode .

% of equivalent amount of AgNO$_3$ added	Potential of Ag/AgBr electrode
0	—
30 %	0·1991 v.
50 %	0·2077
80 %	0·2312
90 %	0·2491
99 %	0·3083
99·9%	0·3676
100·0%	0·4856
101 %	0·4910
110 %	0·5501
150 %	0·5914

VIII-2. Asymmetry potential is 0·0085 v.

VIII-3. At 298 °K, P_{O_2} 4·2 . 10^{-67} atm.
At 2860 °K, P_{O_2} 0·21 atm. = complete dissociation.

VIII-4.   Plot $-\log P + 2A\sqrt{I}$, evaluated from data given, against $\sqrt{I}$ and extrapolate to $I = 0$ for P.

	$-\log P_{D_2O}$	
15 °C.	15·08	
25 °C.	14·71	$\Delta H_{\text{Diss.}} = 14{,}420$ cal. at 25 °C.
35 °C.	14·37	

VIII-5.   Mean $K_S = 6·9 . 10^{-15}$.

VIII-6.   Complex is most probably that in which three equivalents of NH$_2$CH$_2$COO′ are combined with one of Zn^{++}. The dissociation constant is about 10^{-12} over the range $m_1 = 0·050$ to $m_1 = 0·180$.

VIII-7. $E_0 = 0·4789$ v. on the hydrogen scale.

VIII-8. Classical $K = 1 \cdot 98 \cdot 10^{-5}$.
Thermodynamic $K = 1 \cdot 89 \cdot 10^{-5}$.

VIII-9.
$$K_1 = \frac{a_{H^+}[HA^-]\,f_1}{[H_2A]}, \quad K_2 = \frac{a_{H^+}[A^=]\,f_2}{[HA^-]\,f_1}.$$

$$K_1 = \frac{a_{H^+}(L - 2[A^=])\,f_1}{M + [A^=]}, \quad K_2 = \frac{a_{H^+}[A^=]\,f_2}{f_1(L - 2[A^=])}.$$

$$K_1 = \frac{a_{H^+}\left(L - \dfrac{2K_2 f_1 L}{(a_{H^+}f_2 + 2K_2 f_1)}\right)f_1}{M + \dfrac{K_2 f_1 L}{(a_{H^+}f_2 + 2K_2 f_1)}}.$$

$$K_1 M\, a_{H^+} f_2 + K_1 K_2\,(2M f_1 + L f_1) = (a_{H^+})^2 L f_1 f_2.$$

$$2M + L = N,$$

$$\therefore\ (a_{H^+})^2 f_2 \frac{L}{N} = a_{H^+}\frac{f_2}{f_1}\frac{M}{N}K_1 + K_1 K_2.$$

For adipic acid, $pK_1 = 4 \cdot 48$,
$pK_2 = 5 \cdot 42$.

VIII-10. For electroneutrality
$$2[Mg^{++}] + [MgOH^+] + 2[Ba^{++}] + [H^+] = [Cl^-] + [OH^-]$$
$$+ [HCO_3^-] + 2[CO_3^=],$$
and $[Cl^-] = 2[Mg^{++}] + 2[MgOH^+]$.
Hence, the required equation.
The second dissociation constant of $Mg(OH)_2$ is given by
$$K = f_2 \frac{[Mg^{++}][OH^-]}{Mg\,[OH^+]}.$$

The CO_2 content of the solution must be allowed for and activities must be used throughout for accurate results.

g. $(Ba(OH)_2)$	$[MgOH^-] \cdot 10^5$	pK
0·1155	0·595	2·56
0·2110	1·67	2·67
0·6215	6·16	2·69
1·0080	10·00	2·61

CHAPTER IX

IX-1.
$$K_1 = \frac{x}{1-x}[R^{+++}], \qquad x = \frac{..}{[R^{+++}]}.$$

$$K_2 = \frac{4[R^{+++}]^2(x')^2}{1-x'}, \qquad x' = \frac{c_{H^+}}{2[R^{+++}]}.$$

| | Ce | | Y | |
	$K_1 . 10^9$	$K_2 . 10^{15}$	$K_1 . 10^9$	K_2
0·100	1·0	5·0	1740	$8·7 . 10^{-10}$
0·075	1·1	4·7	1400	$2·2 . 10^{-10}$
0·050	1·0	3·5	1100	$1·2 . 10^{-10}$
0·010	0·5	0·6	200	$4·6 . 10^{-11}$
0·005	0·5	0·3	20	$1·0 . 10^{-12}$

Thus the mechanism, $R^{+++} + H_2O \rightleftarrows ROH^{++} + H^+$, appears more probable than for cerium, but yttrium appears to follow neither mechanism well.

IX-2.

	$\log (K_r)_\infty$
Aniline	1·88
o-Toluidine	2·70
m-Toluidine	1·88
p-Toluidine	0·92
p-Chloraniline	3·48
α-Picoline	—0·16
β-Picoline	—0·48
sym-Collidine	—1·94
Quinaldine	0·10
Imidazole	—1·28 .

IX-3. $pK = 1·71.$

The indicator could be used for end points in the range pH 1·5 - 8·0.

IX-4. For an unsymmetrical acid HABH there are two dissociation constants

$$K_1 = \frac{[H^+][ABH^-]}{[HABH]}, \text{ and } K_2 = \frac{[H^+][HAB^-]}{[HABA]}.$$

The experimental constant however is,

$$K' = \frac{[H^+]([ABH^-]+[HAB^-])}{[HABH]},$$

or $\qquad K' = K_1 + K_2.$

For the monoethyl ester,

$$K_\alpha = \frac{[H^+][ABEt^-]}{[HABEt]}, \quad K_\beta = \frac{[H^+][EtAB^-]}{[EtABH]}.$$

If the ester group has a negligible effect on the dissociation of the other end of the molecule,

$$K_1 = K_\alpha, \quad K_2 = K_\beta.$$
$$\therefore \quad K' = K_\alpha + K_\beta.$$

If the acid is symmetrical, $K_\alpha = K_\beta$,

$$\text{and } K' = \frac{K_\alpha}{2};$$

i.e. the first dissociation constant of a symmetrical dibasic acid is twice that of its monoethyl ester.

IX-5. For electroneutrality

$$[B^+] + [H^+] = [OH^-] + [A^-].$$

$$\frac{dc_B}{dpH} - \frac{d[OH^-]}{dp_H} - \frac{d[H^+]}{dp_H} + \frac{d}{dp_H}\left(\frac{K_A c_0}{[H^+] + K_A}\right),$$

$$2\cdot803 \quad [OH^-] + [H^+] + \frac{[H^+]c_0 K_A}{([H^+] + K_A)^2}\right].$$

Maximum buffer capacity when $pH = pK_A$.

If the acid is strong $[A^-] = $ const.

$$\therefore \quad \frac{dc_B}{dpH} = 2\cdot803\,([OH^-] + [H^+]),$$

and the regions of maximum buffer capacity are at very high and very low pH.

IX-6. $\qquad K_1 = \frac{[A_1^-][H^+]}{[HA_1]}, \quad K_2 = \frac{[A_2^-][H^+]}{[HA_2]}.$

Dissociation constants in separate solutions, α and β, and in the same solution, α' and β'.

In separate solution $K_1 \simeq \alpha^2 m_1$, $\quad K_2 \simeq \beta^2 m_2$.

In mixed solution, $\quad K_1 \simeq (\alpha' m_1 + \beta' m_2) \alpha'$,

$$\text{and} \quad \frac{K_1}{K_2} = \frac{\alpha'(1-\beta')}{\beta'(1-\alpha')} \simeq \frac{\alpha'}{\beta'}.$$

$$\therefore \quad \alpha' = \alpha \left(1 + \frac{K_2 m_2}{K_1 m_1}\right)^{-\frac{1}{2}}.$$

When base is added, φ of HA, and $(1-\varphi)$ of HA_2 reacts.

$$\therefore \quad \frac{K_1}{K_2} = \frac{[A_1][HA_2]}{[A_2][HA_1]}.$$

$$[A_1] \simeq m_B \, \varphi.$$

$$[A_2] \simeq m_B (1 - \varphi).$$

$$\therefore \quad \frac{K_1}{K_2} = \frac{\varphi \, [m_2 - m_B (1 - \varphi)]}{(1 - \varphi)(m_1 - m_B \, \varphi)}.$$

IX-7.

		K_2	K_1	ΔH_2 (cal.)	ΔH_1 (cal.)
Glycine:	0°	$4 \cdot 81 \cdot 10^{-11}$	$2 \cdot 66 \cdot 10^{-3}$	10,700	4,500
	20°	$1 \cdot 875 \cdot 10^{-10}$	$4 \cdot 68 \cdot 10^{-3}$		
Alanine:	0°	$3 \cdot 41 \cdot 10^{-11}$	$2 \cdot 66 \cdot 10^{-3}$	11,450	4,500
	20°	$1 \cdot 485 \cdot 10^{-10}$	$4 \cdot 68 \cdot 10^{-3}$		

IX-8. See text for method.

$$K_1 = 4 \cdot 30 \cdot 10^{-3}.$$

$$K_2 = 1 \cdot 22 \cdot 10^{-10}.$$

IX-9.

	r
Malonic	1·5 Å.
Succinic	5·0
Glutaric	9·2
Adipic	11·5
Pimelic	13·2
Suberic	14·5
Azelaic	16·8 .

$r = 4\cdot4 + 1\cdot78m$, when m, the number of carbon atoms between the —COOH groups, is > 2. This suggests that these acids are of a linear, or a linear zig-zag form. For β-n-propyl glutaric acid, $r = 2\cdot12$ Å, which indicates that this acid must have a ring form with the —COOH groups close together,

$$\text{Pr — CH} \underset{\text{CH}_2}{\overset{\text{CH}_2}{\diagup\diagdown}} \overset{\text{COOH}}{\underset{\text{COOH}}{\diagdown\diagup}}$$
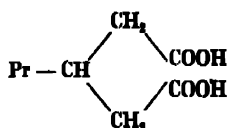
IX-10.   The equation, $w = \sum_{j} \dfrac{q_j e}{\varepsilon}\left(\dfrac{1}{(r_j)_1} - \dfrac{1}{(r_j)_2}\right)$, is simply the change

in energy of the proton which has moved relative to several centres of electrical charge. It may be best evaluated graphically, by means of a scale drawing of the acid molecule.

$$C = -41\cdot9 .$$

For H_3AsO_4, $\log K = -2\cdot5$.
For H_2GeO_3, $\log K = -2\cdot6$.
For H_4GeO_4, $\log K = -7\cdot2$.

∴ H_4GeO_4 appears the more probable structure.

CHAPTER X

X-1.

$e_{(H_2)}$ (v.)	C (μF/cm.^{2}) (graphically)	C (μF/cm.^{2}) (Question 2)
$+0\cdot2$	52	50
$+0\cdot1$	52	50
0	52	50
$-0\cdot1$	52	50
$-0\cdot2$	52	39
$-0\cdot3$	36	41
$-0\cdot4$	21·5	29
$-0\cdot5$	21·5	21
$-0\cdot6$	21·5	20

E_0 (v.)	C (μF/cm.^{2}) (graphically)	C (μF/cm.^{2}) (Question 2)
—0·7	21·5	20
—0·8	21·5	20
—0·9	21·5	20
—1·0	21·5	23
—1·1	21·5	19
—1·2	21·5	

X-2.   This expression is valid only for small values of a, and if C remains constant. It appears to give results in agreement with the graphical method when C is constant and elsewhere to give the general form of the curve. For answer to first part see last column of Question X-1.

e (v.)	C (μF/cm.^{2}) (pure sol.)	C (μF/cm.^{2}) (with AmOH present)
0·4	29	28
0·5	28	27
0·6	28	45·5
0·7	26·4	24
0·8	29	50
0·9	31·5	8·8
1·0	32	8·8
1·1	25·5	6·0
1·2	21·8	8·0
1·3	19·2	11·0
1·4	17·1	31
1·5	16·7	50
1·6	16·2	22
1·7	15·8	21

At 1·2 v., $\dfrac{C_{pure}}{C_{AmOH}} = 7\cdot8$; $\dfrac{\varepsilon_{H_2O}}{\varepsilon_{AmOH}} = 4\cdot9$.

This indicates that the dielectric constant in the double layer is not equal to that in the bulk.

X-3. $C = 22\cdot5 \ \mu$F/cm.^{2} .

X-4.

0·1N HCl		0·01N HCl		0·001N HCl	
$\Delta\psi$	ζ	$\Delta\psi$	ζ	$\Delta\psi$	ζ
—0·89	—0·05	—0·82	—0·10	—0·82	—0·15
—0·51	—0·07	—0·52	—0·12	—0·46	—0·17
—0·72	—0·08	—0·78	—0·14	—0·57	—0·20
—1·26	—0·10	—1·00	—0·15	—0·86	—0·22

Interpolating values at $\Delta\psi = 0\cdot5$, and plotting ψ_1 against $\log[H^+]$ the line is found to have a slope 0·06, in good agreement with the theoretical value 0·058.

X-5.   For a solution containing HCl and LaCl$_3$, STERN's equation becomes,

$$C(\Delta\psi - \zeta) = -zF\left(c_1 e^{\frac{-\zeta_1 F}{RT}} + c_2 e^{\frac{-3\zeta_1 F}{RT}} - c_3 e^{\frac{+\zeta_1 F}{RT}}\right)$$

$$-\sqrt{\frac{\varepsilon RT}{2\pi}}\sqrt{c_1\left(e^{\frac{-\zeta_1 F}{RT}} - 1\right) + c_2\left(e^{\frac{-3\zeta_1 F}{RT}} - 1\right) + c_3\left(e^{\frac{+\zeta_1 F}{RT}} - \right.}$$

where c_1, c_2, c_3, are the concentrations, respectively, of the hydrogen, lanthanum, and chloride ions in g.ions/cm.[3].

[LaCl$_3$]	$\Delta\eta$	ζ_1
0		—0·121 v.
$10^{-5}N$	—0·007 v.	—0·118 v.
$10^{-4}N$	—0·068 v.	—0·083 v.

The change is, therefore, in the direction predicted by the theory although the agreement is not quantitative.

X-6.   The surface excess of alcohol may be represented by $\Gamma = \Gamma_0 e^{-\frac{w}{RT}}$, where w is the work of replacement of a water molecule by an alcohol dipole, given by $\left\{(a_A - a_B)\dfrac{F^2}{2} + (\mu_A - \mu_B)\,F\right\}$ (cf. BUTLER, Proc. Roy. Soc., 1929, A. 122, 399). The surface tension lowering is proportional to the surface excess of alcohol and the field F is proportional to the potential e

$$\therefore \quad \Delta\sigma = \Delta\sigma_0 \, e^{-(ae^2 - be)}.$$

$$a\,e^2 + be = a\,(e - e_{max.})^2 - \frac{b^2}{4a^2},$$

if the potential at which $\Delta\sigma$ is a maximum $(\Delta\sigma_{max.})$ is $e_{max.}$.

$$\therefore \ \ \Delta\sigma = \Delta\sigma_m \, e^{-a\,(e-e_{max.})^2}$$

$\Delta\sigma_m = 49$ GOUY units.

$e_m \ \ = 1\cdot02$ v.

$a \ \ = 8\cdot85$.

X-7.

pH	ζ_e/ζ_0
2	0·93
4	1·04
6	0·98
8	1·01
10	0·99

Thus, the zeta potential appears to be the same when measured by electrophoresis or by electro-osmosis.

X-8. From STOKES' law, the limiting velocity of a sphere falling in a viscous medium is,

$$u = \frac{2\,g\,r^2\,(\varrho' - \varrho)}{9\,\eta}\,.$$

If q is the mobile charge per square centimetre of double layer, the current due to the movement of the particles is,

$$\overrightarrow{I} = 4\,\pi\,r^2\,n\,q\,u\,.$$

In a steady state this is equal to the electrolytic current in the reverse direction,

$$\overleftarrow{I} = \frac{\Delta\psi A\varkappa}{l}\,.$$

$$\therefore \ \Delta\psi = \frac{8\,\pi\,r^4\,n\,q\,g\,l\,(\varrho' - \varrho)}{9\,\eta\,A\,\varkappa}\,.$$

X-9. $$dG = SdT + n_1\,d\mu_1 + n_2\,d\mu_2\ldots.$$

At $T_{const.}$, $$dP = \frac{dG}{V} = \frac{n_1}{V}\,d\mu_1 + \frac{n_2}{V}\,d\mu_2\ldots.,$$

$$= c_{ps.}\,RT\,d\ln a_{ps.} + c_1\,RT\,d\ln a_1 + c_2\,RT\,d\ln a_2\ldots.$$

($c_{pa.}$ is the concentration of protein salt). The ionic concentration outside the membrane is kept constant; hence, the activities of the diffusible components both inside and outside the membrane are constant;

$$i.e., \quad dP = c_{pa.} \; RT \; d\ln a_{pa.} \, .$$

But the activities of the *ions* will not be constant.

$$dP = c_p \, RT \, d\ln a_p + c_a \, RT \, d\ln a_a \ldots + c_i \, RT \, d\ln a_i \, .$$

Membrane equilibrium, $RT \, d\ln a_i = RT \, d\ln a_i' - n_i \, F \, \Delta\psi_m$; or, since a_i' the ionic concentration outside the membrane is constant,

$$RT \, d\ln a_i = - n_i \, F \, E_m \, .$$

Electroneutrality inside membrane,

$$c_p \, n_p = - (c_a \, n_a + \ldots c_i \, n_i) \, .$$

$$\therefore \; dP = c_p \, RT \, d\ln a_p + c_p \, n_p \, RT \, d\!\left(\frac{\Delta\psi_m \, F}{RT}\right).$$

$$\Delta\pi = \Delta\pi_p + \Delta\pi_i \, ;$$

where

$$\Delta\pi_p = RT \int_0^{c_p} c_p \, d\ln a_p \, ,$$

$$\Delta\pi_i = RT \int_0^{u} c_p \, n_p \, du \, .$$

c_p	$\Delta\pi_p =$ mm./Hg
0·000103	1·9
0·000555	11·1
0·001320	27·8
0·00357	96·4
0·00493	163·5

Note: empirically, n_p is found to be directly proportional to $\Delta\psi_m$.

$$\therefore \quad \Delta\pi_i = \text{const.} \, (\Delta\psi_m)^2 \, .$$

X–10. Current due to liquid flow,

$$i' = \frac{\zeta \, \varepsilon \, r_i^2 \, P}{4 \, l \, \eta} \quad \text{(see p. 393).}$$

Electrolytic current, $i = \dfrac{\Delta\psi}{l} (\varkappa_0 \, \pi \, r_i^2 + 2 \, \pi \, r_i \, \varkappa_w) \, .$

In steady state $i = i'$.

$$\therefore \quad \zeta = \frac{4\pi\eta}{\varepsilon}\,\varkappa_0\,\frac{\varDelta\psi}{P}\left(1 + \frac{2\varkappa_w}{r_i\,\varkappa_0}\right).$$

Putting $$\zeta_i = \frac{4\pi\eta}{\varepsilon}\,\varkappa_0\,\frac{\varDelta\psi}{P},$$

$$\zeta = \zeta_i\left(1 + \frac{2\varkappa_w}{r_i\,\varkappa_0}\right).$$

If two tubes of radii r_1, r_2 give values ζ_1, ζ_2 on application of simple theory, then,

$$\varkappa_w = \frac{(\zeta_2 - \zeta_1)\,\varkappa_0}{\left(\dfrac{\zeta_1}{r_1} - \dfrac{\zeta_2}{r_2}\right)\dfrac{}{2}},$$

and $$\zeta = \zeta_1\,\zeta_2\,\frac{\left(\dfrac{1}{r_1} - \dfrac{1}{r_2}\right)}{\left(\dfrac{\zeta_1}{r_1} - \dfrac{\zeta_2}{r_2}\right)}.$$

Hence,

$c \cdot 10^6$	ζ (m.v.)	$\varkappa_w \cdot 10^3$ (mho)
2	—222	1·13
6	—184	1·04
20	—165	1·57
40	—147	1·79
80	—136	3·18

CHAPTER XI

XI-1. $a = 1\cdot288$ v.
        $b = 0\cdot101$ v.
        $i_0 = 1\cdot6 \cdot 10^{-13}$ amp.cm. $^{-1}$.

XI-2.   If change in overpotential is due to concentration changes,

$$1\cdot57 - 0\cdot35 = \frac{RT}{F}\ln\frac{c_1}{c_2}.$$

$$\therefore \quad \frac{c_1}{c_2} = 10^{20.7}.$$

The concentration at the electrode is thus unreasonably small when the current is 10^{-3} amp.cm.$^{-2}$. The theory of MACHU is not supported.

XI-3.   The diffusion current (i_d) may be calculated from the ILKOVIČ equation. It is related to the total limiting current (i_L) in a binary electrolyte by

$$\frac{i_L}{i_d} = \frac{1}{1 - n_+},$$

where n_+ is the transport number of the cation.
Hence, $i_L = 1.44 \cdot 10^{-3}$ amp.cm.$^{-2}$.

$$\eta_c = \frac{RT}{F} \ln \frac{i_L}{i_{L^-}}.$$

At $2 \cdot 10^{-4}$ amp.cm.$^{-2}$, $\eta_c = 0.004$ v.
The rise in overpotential is, thus, not due to concentration overpotential.

XI-4.   Current efficiency, $a = 58.4\%$.

XI-5. $(\partial \ln i / \partial T)_\eta$ is found to be approximately independent of η, and to correspond to a heat of activation of 9.8 cal.

XI-6.   Pressure of atomic hydrogen $= 10^{-11.9}$ atm.
This is equivalent to $2.5 \cdot 10^{-4}$ atoms cm.$^{-2}$ if the layer is 100 Å thick.

$$\text{Velocity} = \frac{i N_A}{F [\text{H}]} = 2.5 \cdot 10^{13} \text{ cm.sec.}^{-1}.$$

The atoms would thus have to travel faster than light, indicating that a literal interpretation of the theory of HICKLING is unsatisfactory.

XI-7.   The limiting current for the first reduction step on the experimental curve for a stationary electrode is ca. $8 \cdot 10^{-5}$ amp.cm.$^{-2}$. If this corresponds to the reaction $As^{+++} \to As$, and the second limiting current to $As \to AsH_3$, then the second limiting current

should be $6 . 10^{-5}$ amp. A curve can then be plotted using the equation

$$E = E_i - \frac{RT}{zF} \ln \frac{i}{i_d - i}.$$

This curve is of the same form as the experimental curve and the horizontal portions occur at approximately the same potentials. The difference between the two limiting currents is very much larger than the theoretical value.

XI-8. If the charge transfer across the double layer occurs at a rate i' when the current is i,

$$i - i' = c \frac{de}{dt}.$$

For steady electrolysis $\dfrac{de}{dt} = 0$ and $i = i'$.

$$i' = i_0 e^{\frac{- a e F}{RT}}.$$

If the current is switched off, $i = 0$,

$$\therefore \quad c \frac{de}{dt} = - i' = - i_0 e^{\frac{- a e F}{RT}}.$$

$$\therefore \quad e^{\frac{a e_0 F}{RT}} - e^{\frac{a e F}{RT}} = \frac{a F}{RT} \frac{i_0 t}{c}.$$

If $e_0 \ll e$ (both are negative),

$$e = \frac{RT}{aF} \ln \frac{aF}{RT} \frac{i_0 t}{c}.$$

$$C = 15 \ \mu F/cm.^2.$$

XI-9. The system can be considered as an electrolytic cell with electrodes of the two components making up the film material, the cell having an internal resistance R_i corresponding to the ionic transport and an external resistance R_s corresponding to the electronic transport. The transport of material across the film is measured by the current flowing,

$$I = \frac{E}{R_s + R_i},$$

where E is the e.m.f. of the "cell".

$$R_s = \frac{y}{A \varkappa n_s},$$

$$R_i = -\frac{y}{A \varkappa (n_c + n_a)},$$

where A is the area of the film.
Hence

$$I = \frac{E A \varkappa n_s (n_c + n_a)}{y}.$$

The rate of growth of the film may then be obtained using
FARADAY's law:

$$\frac{dy}{dt} = \frac{W I}{F} \cdot \frac{1}{A \varrho},$$

which together with the equation for the current and

$$\Delta G = -zFE$$

becomes:

$$\frac{dy}{dt} = -\frac{W \varkappa n_s (n_c + n_a) \Delta G}{z F^2 \varrho} \cdot \frac{1}{y}.$$

(cf. T. P. HOAR and L. E. PRICE, *Trans. Faraday Soc.*, 1938, **34**,
867.)

XI-10.   Resistance of element of solution 1 cm.² area and dx cm. thick,

$$dR = \varrho \, dx,$$

$$= \frac{1}{\varkappa} dx = \frac{1}{Ac} dx.$$

$$i = i_d + i_m = i_d + n_+ i,$$

$$= \frac{F D}{n_-} \cdot \frac{\partial c}{\partial x} + n_+ i.$$

$$i = \frac{FD}{n_-} \frac{\partial c}{\partial x}.$$

$$d\,\eta_{r.d.} = i\,dR = \frac{F\,D}{n_-} \cdot \frac{\partial c}{\partial x} \cdot \frac{1}{\Lambda c}\,dx.$$

$$\eta_{r.d.} = \int_{c_0}^{c_s} \frac{F\,D}{n_-\Lambda} \cdot \frac{dc}{c},$$

where c_s is concentration at the electrode, and c_0 is that in the bulk.

$$\frac{c_s}{c_0} = 1 - \frac{i}{i_d}.$$

$$\eta_{r.d.} = \frac{F\,D}{n_-\Lambda} \ln\left(1 - \frac{i}{i_d}\right).$$

CHAPTER XII

XII-1. 1800 °K., $4{\cdot}7 \cdot 10^{-5}$ amp.   2200 °K., $1{\cdot}4 \cdot 10^{-2}$ amp.
1900 °K., $2{\cdot}4 \cdot 10^{-4}$ amp.   2300 °K., $4{\cdot}2 \cdot 10^{-2}$ amp.
2000 °K., $1{\cdot}1 \cdot 10^{-3}$ amp.   2400 °K., $1{\cdot}2 \cdot 10^{-1}$ amp.
2100 °K., $4{\cdot}1 \cdot 10^{-3}$ amp.

XII-2. At 1500 °K and 1 atm. there are $2{\cdot}3 \cdot 10^{17}$ positive ions, and at 1600 °K and 100 cm. $5{\cdot}25 \cdot 10^{18}$ positive ions. The number formed in this change is $5{\cdot}02 \cdot 10^{18}$.

XII-3. In time dt the ion travels along the tube a distance,

$$dx = v\,dt,$$

if v is the linear velocity of the gas; and also towards the inner electrode,

$$dr = u\,F\,dt,$$

$$\frac{u\,dx}{v} \cdot \frac{\Delta\psi}{r\ln\dfrac{b}{a}}.$$

The volume of gas flowing past a plane in the tube per second is,

$$Q = \int_{a}^{v} 2\pi v r \, dr = \int_{0}^{d} \frac{2\pi \Delta \psi u}{\ln \frac{b}{a}} \, dx.$$

$$\therefore \quad u = \frac{Q \ln \frac{b}{a}}{2\pi \Delta \psi d}.$$

$$u = 1 \cdot 4 \text{ cm.sec.}^{-1} \text{cm.volt}^{-1}$$

XII-4. $-\dfrac{dP}{dx}$ may be considered as the force acting on the n ions in unit volume in the x direction. In an electric field the force is $F e_0 n$, and the resulting velocity is $u F$. Assuming the velocity to be proportional to the driving force,

$$\frac{-\dfrac{dP}{dx}}{F e_0 n} = \frac{v}{u F} = \frac{P v}{D F e_0 n}.$$

$$P = n k T.$$

$$\therefore \quad u = \frac{D e_0}{kT} = \frac{DF}{RT}.$$

$$u = 51 \text{ cm.sec.}^{-1} . \text{ cm.volt}^{-1}.$$

The discrepancy between this value and the experimental value is probably due to the existence of multiple ions.

XII-5.   4,564 positive ions per cm.^{3}.
$\varkappa = 0 \cdot 0021$ mho.cm.$^{-1}$.

XII-6.   Field between plates, $F = \dfrac{\Delta \psi}{d}$.

Force on ion of charge e, $P = \dfrac{\Delta \psi e}{d}$.

Acceleration, $a = \dfrac{\Delta \psi e}{m d}$.

Velocity, $v = \dfrac{\Delta \psi e t}{m d}$.

$v = 4{\cdot}88 \, . \, 10^7$ cm.sec $^{-1}$.

$t = 4{\cdot}56 \, . \, 10^{-7}$ sec.

Energy delivered to second plate $= 1{\cdot}59 \, . \, 10^{-9}$ ergs.

XII-7. If $\tfrac{1}{2} m v_0^2 \geqslant \varDelta \psi \, e$ the ion reaches the second plate.
The electron reaches the second plate delivering to it $8{\cdot}65 \, . \, 10^{-10}$ ergs. The other $6{\cdot}35 \, . \, 10^{-10}$ ergs are transferred to the source of the e.m.f.

XII-8. Acceleration of a-particle is $7{\cdot}24 \, . \, 10^{13}$ cm.sec. $^{-2}$ toward the first electrode. Its velocity at the moment of collision is $1{\cdot}89 \, . \, 10^7$ cm.sec. $^{-1}$, and the collision occurs $8{\cdot}43 \, . \, 10^{-8}$ sec. after the a particle leaves the first electrode. The velocity of the a-particle immediately after the collision is $1{\cdot}80 \, . \, 10^7$ cm.sec. $^{-1}$ towards the second electrode which it reaches $2{\cdot}87 \, . \, 10^{-7}$ sec. after leaving the first electrode.

XII-9. In the equilibrium, $Me \rightleftarrows Me^+ + e_0^-$, at temperature T,

$$\varDelta S = S_+ + S_- - S_{m_e} = \frac{\varDelta H}{T} \, ;$$

if $\varDelta H$ is the heat of ionisation at this temperature and constant pressure.

$$P \, V = k \, N_A \, T \, .$$

$$S = N_A k \left[\tfrac{5}{2} + \ln \frac{kT}{Ph^3} \, (2 \, \pi \, m \, k \, T)^{3/2} \right] \, .$$

$$\therefore \; S_+ - S_{m_e} = N_A \, k \ln \left[\frac{P_{m_e}}{P_+} \left(\frac{m_+}{m_{m_e}} \right)^{3/2} \right] \, ,$$

where P_{m_e}, P_+ are partial pressures. The mass of the ion (m_+) is very nearly equal to that of the atom (m_{m_e}).

$$\therefore \; S_+ - S_{m_e} = k \, N_A \ln \frac{P_{m_e}}{P_+} \, .$$

Hence, $\quad \ln \dfrac{P_+ \, P_-}{P_{m_e}} = -\dfrac{\varDelta H}{k \, N_A \, T} + \ln \left\{ \dfrac{kT}{h^3} \, (2 \, \pi \, m \, kT)^{3/2} \right\} + \tfrac{5}{2} \, .$

$$\Delta H = \Delta U + k N_A T .$$
$$\Delta U = N_A I .$$
$$\therefore \quad \ln K_p = -\frac{I}{kT} + \tfrac{5}{2}\ln T + \tfrac{3}{2} + \ln \frac{k^{5/2}(2\pi m)^{3/2}}{h^3} .$$

XII-10.   The ratio of numbers of atoms, which is proportional to that of P_{m_0} are found using the expression in Question XII - 9, keeping P_+, P_- constant.

SUBJECT INDEX